# Polymers Plus®

POLYMER PROCESS MODELING

Version 3


*With Aspen Plus® 10*

# *User Guide*

VOLUME 1

AspenTech®

## Use of Aspen Plus and This Manual

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# PREFACE

## ABOUT THIS USER GUIDE

This User Guide documents features unique to Polymers Plus. It assumes prior knowledge of basic Aspen Plus capabilities or user access to the Aspen Plus documentation set. If you are using Polymers Plus with Aspen Custom Modeler, please refer to the Aspen Custom Modeler documentation set.

The first chapter in the User Guide provides an introduction to the use of modeling for polymer processes. Subsequent chapters discuss specific Polymers Plus capabilities. The features covered include methodologies for categorizing chemical components and for tracking their properties, physical properties and phase equilibria, polymerization kinetic models, and steady-state flowsheeting. A volume devoted to simulation examples and steady-state and dynamic applications is provided as a complement to this User Guide. See the *Polymers Plus Examples & Application Case Book*. These examples are designed to give you an overall understanding of the steps involved in using Polymers Plus to model specific systems.

# CONTENTS AND ORGANIZATION

The User Guide is divided into two volumes. The main chapters contained in each volume are described below.

| Chapter | Description |
|---|---|
| **Volume 1** | |
| Chapter 1 - Introduction | This chapter describes the basics of polymer process modeling and the steps involved in defining a model in Polymers Plus. |
| Chapter 2 - Polymer Structural Characterization | This chapter describes the methods used for characterizing components. Included are the methodologies for calculating distributions and features for tracking end-use properties. |
| Chapter 3 - Thermodynamic Properties | This chapter describes the physical property methods available in Polymers Plus. An overview of the key issues for polymer systems is also given. |
| Chapter 4 - Polymerization Reactions | This chapter describes the polymerization kinetic models. An overview of the various categories of polymerization kinetic schemes is given. |
| **Volume 2** | |
| Chapter 5 - Steady-State Flowsheeting | This chapter provides an overview of capabilities used in constructing a polymer process flowsheet model. For example, the unit operation models, data fitting tools, and analysis tools, such as sensitivity studies, etc. |
| Chapter 6 - Run-Time Environment | This chapter covers issues concerning the run-time environment including installation issues and troubleshooting tips. |
| Appendices | For the most part the appendices contain data tables referred to in other sections of the manual. |
| Input Language Reference | This section is a tabular summary of the input language for Polymers Plus features. |
| Glossary | This is a compilation of specialized terminology used in polymer process modeling and their definition. |

# OTHER INFORMATION SOURCES

Parts of this User Guide refer to the *Polymers Plus Examples & Applications Case Book*, a complement to this manual. In addition, for information regarding Aspen Plus capabilities not covered in this User Guide, you may need to refer to the *Aspen Plus User Guide* and *Reference Manuals* series for:

- *Unit Operation Models*
- *Physical Property Methods and Models*
- *Physical Property Data*
- *User Models*
- *System Management*

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## Comments and Suggestions

Our goal is to provide you with Polymers Plus documentation that meets your information needs. To help us reach this goal, forward your comments and suggestions to

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For your convenience, a Comments form is included at the end of the User Guide.

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## Glossary

## Index

# 1 INTRODUCTION

This chapter provides an overview of the issues related to polymer manufacturing process modeling and their handling in Polymers Plus®.

Topics covered include:

- About Polymers Plus
- Overview of Polymerization Processes
- Issues of Concern in Polymer Process Modeling
- Polymers Plus Tools
- Defining a Model in Polymers Plus

## ABOUT POLYMERS PLUS

Polymers Plus is a general-purpose process modeling system for the simulation of polymer manufacturing processes. The modeling system includes modules for the estimation of thermophysical properties, and for performing polymerization kinetic calculations and associated mass and energy balances.

Also included in Polymers Plus are modules for:

- Characterizing polymer molecular structure
- Calculating rheological and mechanical properties
- Tracking these properties throughout a flowsheet

There are also many additional features that permit the simulation of the entire manufacturing processes.

# OVERVIEW OF POLYMERIZATION PROCESSES

*Polymer Definition*

A polymer is a macromolecule made up of many smaller repeating units providing linear and branched chain structures. Although a wide variety of polymers are produced naturally, synthetic or man-made polymers can be tailored to satisfy specific needs in the market place, and affect our daily lives at an ever increasing rate. The worldwide production of synthetic polymers, estimated at approximately 100 million tons annually, provides products such as plastics, rubber, fibers, paints, and adhesives used in the manufacture of construction and packaging materials, tires, clothing, and decorative and protective products.

*Polymer Molecular Bonds*

Polymer molecules involve the same chemical bonds and intermolecular forces as other smaller chemical species. However, the interactions are magnified due to the molecular size of the polymers. Also important in polymer production are production rate optimization, waste minimization and compliance to environmental constraints, yield increases and product quality. In addition to these considerations, end-product processing characteristics and properties must be taken into account in the production of polymers (Dotson, 1996).

## Polymer Manufacturing Process Steps

Polymer manufacturing processes are usually divided into the following major steps:

1. Monomer synthesis and purification
2. Polymerization
3. Recovery/Separation
4. Polymer processing (physical and reactive)

The four steps may be carried out by the same manufacturer within a single integrated plant, or specific companies may focus on one or more of these steps (Grulke, 1994).

Figure 1.1 illustrates the important stages for each of these four steps. The main issues of concern for each of those steps are described next.

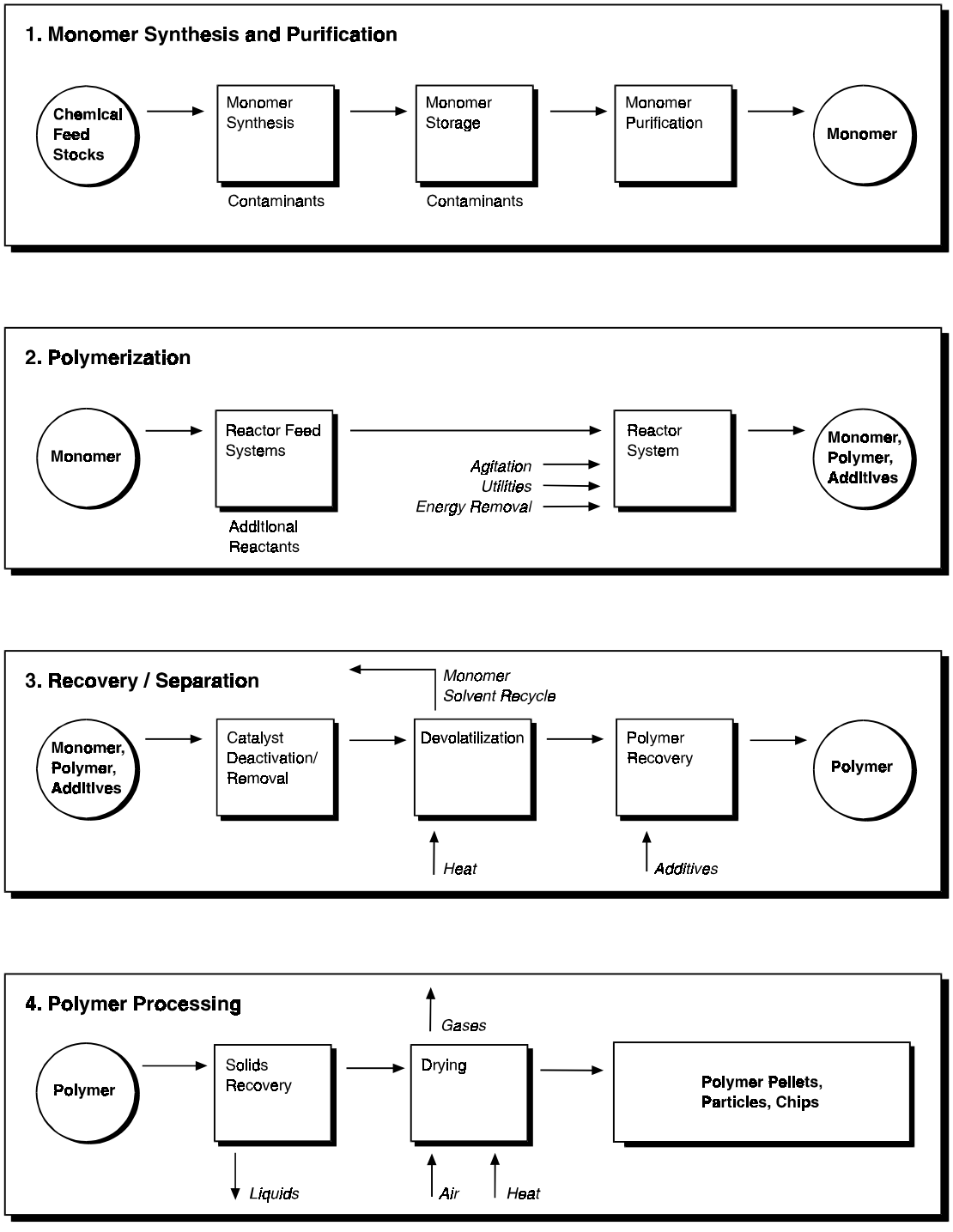


***Figure 1.1*** *Major Steps in Polymer Production Processes*

# ISSUES OF CONCERN IN POLYMER PROCESS MODELING

There are modeling issues associated with each step in the production of polymers. A summary of these issues along with the required tools is listed in Table 1.1.

***Table 1.1 Summary of Polymer Modeling Issues/Concerns***

| Step | Modeling Issues/Concerns | Tools Required |
|---|---|---|
| Monomer synthesis and purification | • Feedstock purity<br>• Monomer degradation<br>• Emissions<br>• Waste disposal | • Unit operations: separators<br>• Reaction kinetics<br>• Phase equilibria |
| Polymerization | • Temperature control<br>• Molecular weight control, polymer specifications<br>• Conversion yield<br>• Reaction medium viscosity<br>• Residence time<br>• Reactor stability<br>• Waste minimization | • Characterization<br>• Reaction kinetics<br>• Phase equilibria<br>• Heat transfer<br>• Unit operations: reactors<br>• Transport phenomena<br>• Process dynamics<br>• Process control |
| Recovery / Separation | • Solvent removal<br>• Monomer recovery | • Unit operations: separators<br>• Phase equilibria<br>• Heat and mass transfer |
| Polymer processing | • Solvent removal<br>• Solids handling | • Heat and mass transfer<br>• Unit operations: separators |

## Monomer Synthesis and Purification

During monomer synthesis and purification, the engineer is concerned with purity. This is because the presence of contaminants, such as water or dissolved gases for example, may adversely affect the subsequent polymerization stage by:

- Poisoning catalysts
- Depleting initiators
- Causing undesirable chain transfer or branching reactions

Another concern of this step is the prevention of monomer degradation through proper handling or the addition of stabilizers. Control of emissions, and waste disposal are also important factors in this step.

## Polymerization

The polymerization step is usually the most important step in terms of the economic viability of the manufacturing process. The desired outcome for this step is a polymer product with specified properties such as:

- Molecular weight distribution
- Melt index
- Composition
- Crystallinity/density
- Viscosity

The obstacles that must be overcome to reach this goal depend on both the mechanism of polymer synthesis (chain growth or step growth), and on the polymerization process used.

Polymerization processes may be batch, semi-batch or continuous. In addition, they may be carried out in bulk, solution, slurry, gas-phase, suspension or emulsion. Batch and semi-batch processes are preferred for specialty grade polymers. Continuous processes are usually used to manufacture large volume commodity polymers. Productivity depends on heat removal rates and monomer conversion levels achieved. Viscosity of polymer solutions, and polymer particle suspensions and mixing are important considerations. These factors influence the choice of, for example, bulk versus solution versus slurry polymerization. Another example is the choice of emulsion polymerization that is often dictated by the form of the end-use product, water-based coating or adhesive. Other important considerations may include health, safety and environmental impact.

Most polymerizations are highly exothermic, some involve monomers which are known carcinogens and others may have to deal with contaminated water.

In summary, for the polymerization step, the reactions which occur usually cause dramatic changes in the reaction medium (e.g. significant viscosity increases may occur), which in turn make high conversion kinetics, residence-time distribution, agitation and heat transfer the most important issues for the majority of process types.

## Recovery / Separation

The recovery/separation step can be considered the step where the desired polymer produced is further purified or isolated from by-products or residual reactants. In this step, monomers and solvents are separated and purified for recycle or resale. The important concerns for this step are heat and mass transfer.

## Polymer Processing

The last step, polymer processing, can also be considered a recovery step. In this step, the polymer slurry is turned into solid pellets or chips. Heat of vaporization is an important factor in this step (Grulke, 1994).

## Summary

In summary, production rate optimization, waste minimization and compliance to environmental constraints, yield increase, and product quality are also important issues in the production of polymers. In addition, process dynamics and stability constitute important factors primarily for reactors.

# POLYMERS PLUS TOOLS

Polymers Plus provides the tools that allow polymer manufacturers to capture the benefits of process modeling.

Polymers Plus can be used to build models for representing processes in two modes: with Aspen Plus® for steady-state models, and with Aspen Custom Modeler™ for dynamic models. In both cases, the tools used specifically for representing polymer systems fall into four categories:

1. Polymer characterization
2. Physical properties
3. Reaction kinetics
4. Data

Through Aspen Plus and Aspen Custom Modeler, Polymers Plus provides robust and efficient algorithms for handling:

- Flowsheet convergence and optimization
- Complex separation and reaction problems
- User customization through an open architecture

## Component Characterization

Characterization of a polymer component poses some unique challenges. For example, the polymer component is not a single species but a mixture of many species. Properties such as molecular weight and copolymer composition are not necessarily constant and may vary throughout the flowsheet and with time. Polymers Plus provides a flexible methodology for characterizing polymer components.†

Each polymer is considered to be made up of a series of segments. Segments have a fixed structure. The changing nature of the polymer is accounted for by the specification of the number and type of segments it contains at a given processing step.

Each polymer component has associated attributes used to store information on molecular structure and distributions, product properties, and particle size when necessary. The polymer attributes are solved/integrated together with the material and energy balances in the unit operation models.

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† U.S. Patent No. 5,687,090

## Polymer Physical Properties

Correlative and predictive models are available in Polymers Plus for representing the thermophysical properties of a polymer system, the phase equilibrium, and the transport phenomena. Several physical property methods combining these models are available. In addition to the built-in thermodynamic models, the open-architecture design allows users to override the existing models with their own in-house models.

## Polymerization Kinetics

The polymerization step represents the most important stage in polymer processes. In this step, kinetics play a crucial role. Polymers Plus provides built-in kinetic mechanisms for several chain-growth and step-growth type polymerization processes. The mechanisms are based on well established sources from the open literature, and have been extensively used and validated against data during modeling projects of industrial polymerization reactors.

There are also models for representing polymer modification reactions, and for modeling standard chemical kinetics. In addition to the built-in kinetic mechanisms, the open-architecture design allows users to specify additional reactions, or to override the built-in mechanisms.

## Modeling Data

A key factor in the development of a successful simulation model is the use of accurate thermodynamic data for representing the physical properties of the system, and of kinetic rate constant data which provide a good match against observed trends.

In order to provide the physical property models with the parameters necessary for property calculations, Polymers Plus has property parameter databanks available. These include:

- Polymer databank containing parameters independent of chain length
- Segment databank containing parameters to which composition and chain length are applied for polymer property calculations
- Functional group databank containing parameters for models using a group contribution approach is also included

This User Guide contains several tabulated parameters which may be used as starting values for specific property models. Property data packages are also being compiled for some polymerization processes and will be made available in future versions.

In addition to physical property data, Polymers Plus provides users with ways of estimating missing reaction rate constant data. For example, the data regression tool can be used to fit rate constants against molecular weight data.

## Process Flowsheeting

Polymers Plus provides unit operation models, flowsheeting options, and analysis tools for a complete representation of a process.

Models for batch, semi-batch and continuous reactors with mixing extremes of plug flow to backmix are available. In addition, other unit operation models essential for flowsheet modeling are available such as:

- Mixers
- Flow splitters
- Flash tanks
- Devolatilization units

Flowsheet connectivity and sequencing is handled in a straight forward manner.

Several analysis tools are available for applying the simulation models developed. These include tools for:

- Process optimization
- Examining process alternatives as case studies
- Analyzing the sensitivities of key process variables on polymer product properties
- Fitting process variables to meet design specifications

# DEFINING A MODEL IN POLYMERS PLUS

In order to build a model of a polymer process you must already be familiar with Aspen Plus. Therefore, only the steps specific to polymer systems will be described in detail later in this User Guide. The steps for defining a model in Polymers Plus are as follows:

**Step 1. Specifying Global Simulation Options**

The first step in defining the model is the specification of:

- Global simulation options, i.e. simulation type
- Units to be used for simulation inputs and results
- Basis for flowrates
- Maximum simulation times
- Diagnostic options

**Step 2. Defining the Flowsheet**

For a full flowsheet model, the next step is the flowsheet definition. Here you would specify the unit operation models contained in the flowsheet and define their connectivity.

Chapter 5 describes the unit operation models available for building a flowsheet.

**Step 3. Defining Components**

Most simulation types require a definition of the component system. You must correctly identify polymers, polymer segments, and oligomers as such. All other components are considered conventional by default.

Chapter 2 provides information on defining components.

**Step 4. Characterizing Components**

Conventional components in the system are categorized by type. Additional characterization information is required for other than conventional components. You must specify the:

- Component attributes to be tracked for polymers
- Type of segments present
- Structure of oligomers
- Type and activity of catalysts

In addition, you may wish to request tracking of molecular weight distribution.

Component characterization is discussed in Chapter 2.

**Step 5. Specifying Property Models**

You must select the models to be used to represent the physical properties of your system.

Chapter 3 describes the options available for specifying physical property models.

**Step 6. Defining Polymerization Kinetics**

Once you have made selections out of the built-in polymerization kinetic models to represent your reaction system, you need to choose specific reactions from the sets available and enter rate constant parameters for these reactions.

Chapter 4 describes the models available and provides descriptions of the input options.

**Step 7. Defining Feed Streams**

For flowsheet simulations, you must enter the conditions of the process feed streams. If the feed streams contain polymers, you must initialize the polymer attributes.

Polymer attribute definition in streams is discussed in a separate section of Chapter 2.

**Step 8. Specifying UOS Model Operating Conditions**

You must specify the configuration and operating condition for unit operation models contained in the flowsheet. In the case of reactors, you have the option of assigning kinetic models defined in step 6 to specific reactors.

Chapter 5 provides some general information regarding the use of unit operation models.

**Step 9. Specifying Additional Simulation Options**

For a basic simulation the input information you are required to enter in steps 1-8 is sufficient. However, there are many more advanced simulation options you may wish to add in order to refine or apply your model. These include setting up the model for plant data fitting, sensitivity analyses, etc.

Many of these options are described in a separate section of Chapter 5.

Information for building dynamic models is given in the Aspen Custom Modeler documentation set. Note that for building dynamic models, users must first build a steady-state model containing:

- Definition of the polymer system in terms of components present
- Physical property models
- Polymerization kinetic models

Polymers Plus setup and configuration instructions are given in Chapter 6.

# REFERENCES

Dotson, N. A., R. Galván, R. L. Laurence, M. Tirrell, Polymerization Process Modeling, VCH Publishers, New York (1996).

Grulke, E. A., Polymer Process Engineering, Prentice Hall, Englewood Cliffs, New Jersey (1994).

Odian, George, Principles of Polymerization, 3rd ed. John Wiley and Sons, New York (1991).

# 2 POLYMER STRUCTURAL CHARACTERIZATION

One of the fundamental aspects of modeling polymer systems is the handling of the molecular structure information of polymers. This chapter discusses the approaches used to address this issue in Polymers Plus.

Topics covered include:

- Polymer Structure
- Polymer Structural Properties
- Characterization Approach

Following this chapter are several sections devoted to the specification of polymer structural characterization information.


| SECTIONS | PAGE |
|---|---|
| 2.1 Component Classification | (2-7) |
| 2.2 Polymer Structural Properties | (2-19) |
| 2.3 Structural Property Distributions | (2-41) |
| 2.4 End-Use Properties | (2-59) |

# POLYMER STRUCTURE

Polymers can be defined as large molecules or macromolecules where a smaller constituting structure repeats itself along a chain. For this reason, polymers tend to exhibit different physical behavior than small molecules also called *monomers*. Synthetic polymers are produced when monomers bond together through polymerization and become the repeating structure or *segment* within a chain. When two or more monomers bond together, a polymer is formed. Small polymer chains containing 20 or less repeating units are usually called *oligomers*.

The fact that identifiable segments are found repeatedly along a polymer chain, provides convenient ways to categorize polymers. Polymers can be classified based on segment composition or sequence:

- Homopolymers - containing one type of repeating unit which can be mapped into one segment
- Copolymers - which have two or more repeating units. Copolymers can be in a random, alternating, block, or graft configuration

If we consider the arrangement of a given chain, another classification arises. Polymers may be:

- Linear
- Branched (with short or long chains)
- Star
- Ladder
- Network

Another classification which results from polymer structure has to do with physical state. A solid polymer may be:

- Amorphous - when the chains are not arranged in a particular pattern
- Crystalline - when the chains are arranged in a regular pattern.

A related classification divides polymers by thermal and mechanical properties into:

- Thermoplastics (may go from solid to melt and vice versa)
- Thermosets (remain solid through heating)
- Elastomers (which have elastic properties)

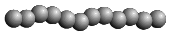
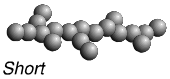
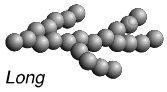
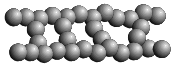
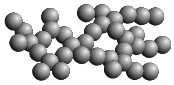
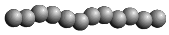
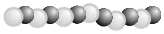
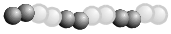
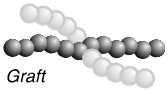
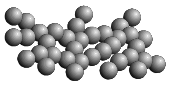
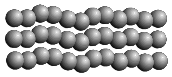
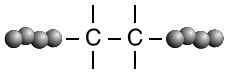
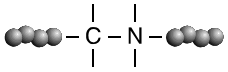
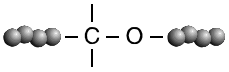
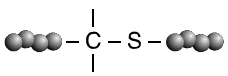
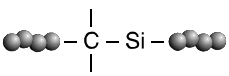
Finally, polymers can be categorized based on the form they are manufactured into: plastics, fibers, film, coatings, adhesives, foams, and composites.

Table 2.1 illustrates the various polymer types based on chain structure and Table 2.2 illustrates the various polymer types based on properties. In addition to these classifications, polymers can be categorized based on the type of constituting atoms on the chains.

Homochains produced through chain-growth polymerization have only carbon atoms on the polymer backbone.

Heterochains produced through step-growth polymerization have other types of atom incorporated into the polymer backbone.

### *Table 2.1 Major Polymer Types by Physical Structure*

| CLASSIFICATION | TYPE | PHYSICAL STRUCTURE |
|---|---|---|
| **Chain Structure** | Linear |  |
| | Branched |  *Short*  *Long* |
| | Star |  |
| | Ladder |  |
| | Network |  |
| **Composition/ Segment Sequence** | Homopolymer |  |
| | Copolymer |  *Alternating*  *Block*  *Graft* |
| **Physical State** | Amorphous |  |
| | Crystalline |  |
| **Backbone Structure** | Homochains *Carbon Only Backbone* |  |
| | Heterochains *Carbon and Other Atoms in Backbone* |     |

### *Table 2.2 Major Polymer Types by Property*

| Classification | Type | Physical Property |
|---|---|---|
| Thermal / Mechanical properties | Thermoplastics | Can melt and solidify again |
| | Thermosets | Remain solid through heating |
| | Elastomers | Have elastic properties |
| Fabrication | Plastics | Very versatile in terms of application |
| | Fibers | Most commonly used as textiles |
| | Coatings | Used for both decorative and protective purposes |
| | Adhesives | Used for their bonding properties |
| | Foams | Used as packaging, upholstery, insulation, etc. |
| | Composites | Can be tailored to many applications |
| | Elastomers | Used for their elastic properties |

Table 2.3 lists various homochain and heterochain polymers based on the type of atoms on the polymer backbone or the substituted side groups.

### *Table 2.3 Major Polymer Categories by Chemical Structure*

| Polymer Category | Description | Examples |
|---|---|---|
| **Polymers with carbon-carbon backbone** | | |
| Polyacrylics | Ethylene backbone with one acrylic acid (or derivative) as side group per ethylene | Polyacrylic acid, polymethyl methacrylate, polyacrylonitrile, polyacrylamide |
| Polydienes | One double bond per repeat unit | Polybutadiene |
| Polyhalogen hydrocarbons | Fluorine or chlorine side group per ethylene | Polyvinyl fluoride, polyvinylidene fluoride, polyvinylchloride, |
| Polyolefins | Alphatic or aromatic substituents | Polyethylene, polypropylene, polyisobutylene, polystyrene |
| Polyvinyls | From vinyl monomers | Polyvinyl acetate, polyvinyl alcohol |
| **Polymers with carbon-nitrogen backbone** | | |
| Polyamides | Amide group on backbone | Nylon 6, nylon 6,6 |
| Polyurethanes | Urethane group on backbone | Polyurethane foams |
| Polyureas | Urea group on backbone | Polyurea resins |
| **Polymers with carbon-oxygen backbone** | | |
| Polyacetals | Acetal group on backbone | Polyacetate |
| Polyethers | Ether group on backbone | Polyethylene oxide, polyphenylene oxide |
| Polyesters | Ester group on backbone | Polycarbonate polyethylene therephthalate, polybutylene therephthalate polylactide |
| **Polymers with carbon-sulfur backbone** | | |
| Polysulfides | Sulfide group on backbone | Polysulfide fibers |

# POLYMER STRUCTURAL PROPERTIES

All the methods of categorizing polymers point to certain key characteristics that must be taken into account in order to fully define polymer molecules. Typical information needed to capture the structure and behavior of polymers includes:

- Chemical structure of segments: segment type, and configuration
- Chain size for the mixture of polymer chains
- Crystallinity
- Additional structural, thermal, and mechanical characteristics

# CHARACTERIZATION APPROACH

Polymers Plus allows for the different types of chemical species that may be found in a polymer system:

- Monomers
- Solvents
- Catalysts
- Oligomers
- Polymers

Polymer segments are introduced to identify the chemical structure of the polymer or oligomer repeat unit. In addition, they are used as building blocks within polymerization reactions, and in the determination of thermodynamic properties.

More than the chemical structure of the segments is needed in order to define a polymer. Also needed is the segment composition of the chains. In addition, properties related to size are needed: degree of polymerization or number of segments.

## Component Attributes

Within Polymers Plus, component attributes are used to define these structural characteristics. Component attributes are available to track segment composition, degree of polymerization, molecular weight, etc. Because the polymer is a mixture of chains, there is normally a distribution of these structural characteristics. The component attributes are used to track the averages.

There are additional attributes used to track information about the distribution of chain sizes. These are the moments of chain length distribution. Detailed information about component attributes is given in Section 2.2.

In addition to the component attributes, users have the option within Polymers Plus to examine polymer molecular weight distribution. This feature is based on a method of instantaneous properties and is described in Section 2.3.

# REFERENCES

Grulke, E. A., Polymer Process Engineering, Prentice Hall, Englewood Cliffs, New Jersey (1994).

Munk, P., Introduction to Macromolecular Science, John Wiley and Sons, New York (1989).

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Rudin, A., The Elements of Polymer Science and Engineering, Academic Press, Orlando Florida (1982).

# 2.1 COMPONENT CLASSIFICATION

This section discusses the specification of components in a simulation model.

Topic covered include:

- Component Categories
- Component Databanks
- Segment Methodology
- Specifying Components

## COMPONENT CATEGORIES

When developing a simulation model in Polymers Plus, users must assign components present in process flow streams to one of the following categories:

- Conventional
- Polymer
- Oligomer
- Segment
- Site-based

Figure 2.1 illustrates the different categories of components and their input requirements.

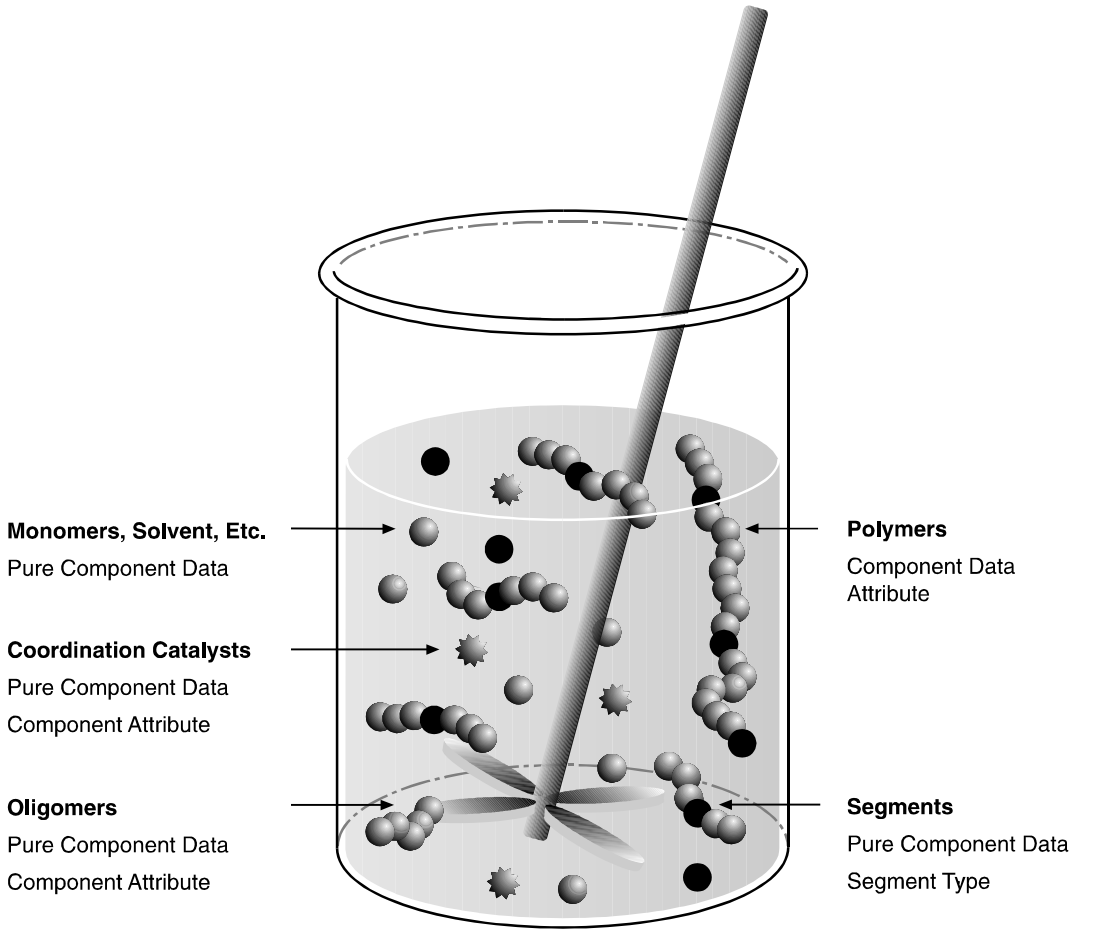


***Figure 2.1*** *Component Types and Input Requirements*

## Conventional Components

Standard conventional components are molecular components such as water. These components have a fixed molecular structure and participate in phase equilibrium. Components falling into this category include:

- Monomers
- Initiators
- Chain transfer agents
- Solvents
- Catalysts

In order to fully specify conventional components, you need only specify pure component data required for the phase equilibrium calculations. This data may be entered or retrieved from component databanks.

Ziegler-Natta catalysts and ionic initiators require additional characterization information.

## Polymers

In Polymers Plus, polymer components represent a distribution of polymeric species. The average size and composition of the molecules in this distribution can change throughout the simulation. Each polymer molecule is considered to be made up of repeating units or segments. Typically, the segments correspond to the monomers which are used to grow the polymer.

The structure of polymers depends on the number and type of segments they contain and the arrangement of segments in linear, branched, or cross-linked forms.

Component attributes are used to track polymer structural properties such as†:

- Segment composition
- Degree of polymerization
- Molecular weight
- Branching
- Moments of molecular weight distribution

Segments are specified independently from polymers. For each polymer, you must select the types of component attributes to be included in the simulation model. If the polymer is present in the process feed streams, you must provide its properties by initializing the component attributes while specifying input data for these feed streams.

Component attribute specification is discussed in Section 2.2.

## Oligomers

By convention, oligomers are defined as components with two or more segments and a fixed molecular structure. They can be defined as volatile or non-volatile. Typically, the oligomer feature is used to allow users to track the loss of volatile short-chain polymers.

In order to specify oligomers, you must specify their composition in terms of the number and type of segments they contain. Oligomers do not require component attributes. For this reason, you may treat a polymer as an oligomer in cases where you want to process the polymer within a unit operation model which cannot handle polymer component attribute data.

Not all kinetic models track oligomers as separate components. If a model does not provide fields for specifying oligomers on its input forms, then these components are not tracked.

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† U.S. Patent No. 5,687,090

## Segments

Segments are the structural units of a polymer or oligomer and are specified independently from these components. Their structure is fixed throughout a simulation. Segments typically correspond to the monomers used to grow the polymer. They are divided into types depending on their location on the polymer chain:

- Repeat units
- End groups
- Branch point (attached to three or four branches)

## Site-Based

Site-based components pertain to multisite reaction kinetic models (Ziegler-Natta and Ionic). Site-based components include Ziegler-Natta catalysts and ionic initiators.

### Ziegler-Natta Catalysts

Ziegler-Natta catalysts are often used to initiate polymer chain formation in chain-growth polymerization reactions. Catalysts can be treated as standard conventional components. Ziegler-Natta catalysts or metallocene catalysts involve one or more polymerization site types which may be in an activated or deactivated state.

In order to use Ziegler-Natta catalysts, you must specify the number of site types and the catalyst properties to be tracked, i.e. the site activity.

Catalyst properties are defined as component attributes. You must initialize the catalyst properties while specifying input data for the streams containing the catalysts.

Component attribute specification is discussed in Section 2.2.

### Ionic Initiators

Ionic initiators are used in anionic and cationic polymerization. The ionic initiators can be treated as standard conventional components. The propagating species in ionic polymerization can be:

- Free-ions
- Ion-pairs
- Dormant esters

In Polymers Plus, these different species are modeled as different sites of an ionic initiator. Three different site-based attributes are tracked for an ionic initiator which are discussed later in Section 2.2.

# COMPONENT DATABANKS

The thermodynamic and transport property models needed to perform the physical property and phase equilibrium calculations during a simulation require pure component property data. These include:

- Molecular weight
- Heat capacity
- Heat of formation
- Heat of vaporization
- Vapor pressure
- Density

Enter that information while selecting and specifying physical property models. Normally, you would make use of the pure component databanks and retrieve data from them for each of the components present in the simulation model:

- Data for conventional components are retrieved from the Pure Component databank
- Data for polymers are retrieved from the POLYMER databank
- Data for oligomers are retrieved either from the pure component databank or from the POLYMER databank
- Data for segments are retrieved from the SEGMENT databank

Descriptions of the databanks, and the parameters they contain are given in Appendix A.

## Pure Component Databank

In the Pure Component databank, components are named using a nomenclature developed for Aspen Plus. Each component is given an alias summarizing the number of each type of atom: C, H, O, N, P, S, CL, F, etc. (e.g. C2H4 for ethylene). For cases where the same alias matches several components, a counter is added to make the distinction (e.g. C2H4O2-1 for acetic acid).

Catalysts are often solid components and may not be found in the PURECOMP databank. Normally, you do not need a rigorous representation of these components. An acceptable approach is to assign a monomer alias to the catalyst and then provide the correct molecular weight and certain parameters which will prevent the catalyst from vaporizing. If an activity coefficient model is being used for phase equilibrium representation, the catalysts can be assumed to be non-volatile by specifying -40 as the first Antoine parameter (PLXANT(1) = -40).

## Segment Databank

In the Segment Databank, a segment name comes from the name of the monomer from which it originates. Therefore, in this databank component names and aliases follow the same conventions as those for the Pure Component Databank.

A label is added to the monomer name to identify the segment as either a repeat unit,-R, an end group,-E, or a branch point, -B (e.g. for butadiene segments: C4H6–R–1or BUTADIENE–R–1 corresponding to the repeat unit $—CH_2—CH=CH—CH_2—$ , C4H5–E–1 or BUTADIENE–E–1 corresponding to the end group $—CH=CH—CH=CH_2$ and C4H5–B or BUTADIENE–B corresponding to the branch segment $—CH_2—CH=CH—CH<$ ).

## Polymer Databank

The Polymer Databank does not follow the conventional nomenclature. The polymer aliases are the typical acronyms used in industry or academia, and the polymer names consist of the repeat unit name enclosed in parentheses and preceded by the prefix Poly (e.g. PS or POLY(STYRENE) for polystyrene).

The MW property parameter used to store molecular weights in the component databanks is the true molecular weight for all component types except polymers. For polymers, the true polymer molecular weight is normally tracked as a component attribute only. The molecular weight stored in the databank is the apparent molecular weight calculated as the average segment molecular weight (See Appendix A).

# SEGMENT METHODOLOGY

The segment approach to characterizing components is a fundamental methodology which affects almost every functionality within Polymers Plus. Segments are used as the building blocks for polymers. Once you have specified the types of segments in the polymer, the segment composition and degree of polymerizationdefined as component attributes may be used to define the size and composition of the polymer.

For oligomers, although component attributes are not used, the number of each segment must be specified directly.

Most of the Polymers Plus physical property models calculate polymer and oligomer properties from segment properties. This is done by taking into account the degree of polymerization ant the segment composition. The calculated properties should be the same for both oligomers and polymers, assuming that the oligomer structure and molecular weight were specified correctly. Note that this is true for mass-based properties only. Mole-based properties will be different between polymer and oligomer if their apparent molecular weights are different.

Within the polymerization reaction models, segments also play a key role. As polymerization progresses, the models map the reacting monomers into the corresponding segments and return rates of change for the segment composition.

# SPECIFYING COMPONENTS

To specify components within your model you will need to know the following:

| Item | For |
|---|---|
| Component types | All the species in your system |
| Property parameter databank selections | The species in the system |
| IUPAC names | All conventional components or you need their physical properties (molecular weight, boiling point, Antoine constants, etc.) |
| Segment structure | All polymers and oligomers (define whether you want to include any end groups or branch points) |
| Polymer properties to be tracked | All polymers, i.e. degree of polymerization, segment composition |
| Additional characteristics | All additional characteristics for catalysts, or ionic initiators |

## Selecting Databanks

For a Polymers Plus simulation, the databanks from which physical property data are generally retrieved are the:

- Pure component databank (PURE10)
- Polymer databank (POLYMER)
- Polymer segment databank (SEGMENT)

Other databanks available in Aspen Plus, user databanks, and in-house databanks may also be accessed if necessary. Descriptions of the polymer and segment databanks, and the parameters they contain are in Appendix A.

If you selected a polymer template to start up your simulation, the correct databanks are already specified.

If you did not select a polymer template, or if you would like to modify the databank selection:

1. From the Data Browser, find the **Components** folder.
2. From the **Components** folder, go to **Specifications**.
3. On the **Selection** tab sheet, click on the **Databanks** tab to open up the databank selection form.

## Defining Component Names and Types

You must specify a:

- Name and a type for each component in the simulation
- Component name or identifier
- Databank name or formula which will set the pure component properties for the component
- Component type which will set the category to which the component belongs and will determine the treatment of that component

To access the components specifications input sheet:

1. From the Data Browser, find the **Components** folder.
2. From the **Components** folder, go to **Specifications**.
3. On the **Selection** tab sheet, click on the **Databanks** tab to set the databanks to be searched for pure component properties.

To define component names and types:

1. On the **Selection** tab sheet, in the **Component ID** field, specify an ID for each component.

   This ID is used to refer to the component in all subsequent input, and is also used to identify the component in the simulation report.

2. For polymers, oligomers, and segments, specify the component type in the **Type** field.

   By default, all components are assumed to be standard conventional components. For Polymers Plus simulation you must correctly identify the component types:

| Use | For |
|---|---|
| Conventional | Standard conventional components |
| Polymer | Homo and copolymers |
| Oligomer | Short chain polymer molecules |
| Segment | Polymer or oligomer repeat units |

3. If component property data are to be retrieved from databanks, you must also supply either the databank component formula in the **Formula** field, or the databank name in the **Component name** field.

## Specifying Segments

The type of each polymer or oligomer segment must be specified on the Polymer Characterization Segments sheet. Segments may be repeat units, end groups or branch points attached to three or four branches.

To access the segments definition input form:

1. From the Data Browser, find the **Components** folder.
2. From the **Components** folder, go to **Polymers**.
3. From the **Polymers** folder, go to **Characterization**.

To define segments:

On the **Segments** tab sheet assign a type to the segments from the **Type** pull-down list.

## Specifying Polymers

For each polymer you must define the component attributes to be tracked. All components specified Polymer in the **Components Specifications** folder require component attributes.

To access the Polymers input specifications:

1. From the Data Browser, find the **Components** folder.
2. From the **Components** folder, go to **Polymers**.
3. From the **Polymers** folder, go to **Characterization**.
4. From the **Characterization** form, click on the **Polymers** tab.

To specify component attributes for the polymers in your simulation:

1. In the **Polymer ID** field, select the desired polymer.
2. If you want to retrieve a predefined set of component attributes, in **Built-in attribute group** select a grouping. The attribute summary table is filled out.

   For a complete discussion of Polymers Plus component attributes, see Section 2.2.

   – or –

   If you do not want to use a predefined set of attributes, or if you would like to change the attribute selection for a given group, click on the attribute table or click on **Edit** to open the attribute list.
3. Click on specific attributes to add or remove from the list.
4. Repeat these steps for each polymer.

## Specifying Oligomers

For each oligomer you must specify an ID and a structure in terms of number and name of contained segments.

To access the oligomers definition input form:

1. From the Data Browser, find the **Components** folder.
2. From the **Components** folder, go to **Polymers**.
3. From the **Polymers** folder, go to **Characterization**.
4. From the **Characterization** form, click on the **Oligomers** tab.

To define oligomers:

1. In the **Oligomer** field, select the desired oligomer.
2. In the **Segment** field, enter the name of a segment contained in the oligomer.
3. Repeat these steps for each oligomer.

You may define as many segments as needed for an oligomer.

## Specifying Site-Based Components

Specify the structure and activity of site-based catalytic species such as Ziegler-Natta catalysts and ionic initiators.

To access the site-based species definition form:

1. From the Data Browser, find the **Components** folder.
2. From the **Components** folder, go to **Polymers**.
3. From the **Polymers** folder, go to **Characterization**.
4. From the **Characterization** form, click on the **Site-Based Species** tab.

To specify site-based species characteristics:

1. Select the component type:  Ziegler-Natta catalyst, ionic initiator, etc.
2. In the **Comp ID** field specify the component name.
3. Specify the number of site types in **Number of sites** for the component. For Ziegler-Natta catalysts, you must also specify the moles of sites per gram of catalyst.
4. Select the list of properties or component attributes to be tracked for that component. Click on the attribute list table or **Edit** to open the attribute list. Click on specific attributes to add or remove them from the list for the component.

# REFERENCES

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Danner R. P., and M. S. High, Handbook of Polymer Solution Thermodynamics, Design Institute for Physical Property Data, American Institute of Chemical Engineers (1992).

Kroschwitz, J., ed., Concise Encyclopedia of Polymer Science and Engineering, John Wiley and Sons, New York (1990).

# 2.2 POLYMER STRUCTURAL PROPERTIES

This section discusses the use of component attributes for tracking polymer structural properties in a simulation model.

Topics covered include:

- Structural Properties as Component Attributes
- Component Attribute Classes
- Component Attribute Categories
- Component Attribute Initialization
- Specifying Component Attributes

## STRUCTURAL PROPERTIES AS COMPONENT ATTRIBUTES

Component attributes provide a convenient framework to associate structural characterization data to components in a flow stream. They are carried throughout the flowsheet along with state and composition information, and effectively extend the stream structure.

Polymers Plus uses component attributes as a vehicle for tracking important modeling information for polymers, ionic initiators and Ziegler-Natta catalysts†. For example, there are component attributes to store:

- Segment composition (segment fraction or segment flow)
- Degree of polymerization (number, weight, and z-average)
- Molecular weight (number, weight, and z-average)
- Degree of branching (long and short)
- Live polymer properties
- Aggregate polymer properties

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† U.S. Patent No. 5,687,090

In the case of multi-site-type Ziegler-Natta catalyst polymerization, the attributes provide the structure to store the properties by site. Examples of catalyst attributes include the fraction of dead and potential sites. The catalyst attributes are used to track catalyst activity. There are also component attributes available to track user defined data.

The complete list of available attributes is given in Tables 2.5-2.10 and Table 2.12, Table 2.13 and Table 2.14.

# COMPONENT ATTRIBUTE CLASSES

Component attributes are divided into classes to reflect the nature of various structural properties carried in process streams:

- Class 0 component attributes are derived quantities from other attributes. They are therefore recalculated from these attributes after they are updated. For example, number average degree of polymerization is a Class 0 component attribute. It is computed from the zeroth and the first moments of chain length distribution.
- Class 1 component attributes are structural properties per unit mass. They are not used for polymers.
- Class 2 component attributes are structural properties per unit time. Examples are zeroth and first moments of chain length distribution

Table 2.4 lists the differences between the attribute classes.

For a typical polymer process simulation, Class 0 and Class 2 component attributes are used. Since Class 0 component attributes are calculated from Class 2 attributes, users have the option of entering either of the two types for simulation models where polymer is present in the process feed streams. For this reason, an attribute initialization scheme has been designed. Component attribute initialization is described later in this section.

***Table 2.4 Polymers Plus Component Attribute Classes***

| Class | Conserved Quantity | Convergence Treatment | Unit of Measurement | Examples |
|---|---|---|---|---|
| 0 | N/A | Recalculated | Varies | Degree of polymerization |
| 1 | Attribute × component mass | Direct substitution | Attribute / component mass | None for polymers |
| 2 | Attribute | Accelerated convergence | Attribute / time | Segment flows, moments of chain length distribution |

# COMPONENT ATTRIBUTE CATEGORIES

The main categories of component attributes available are:

- Polymer attributes
- Ziegler-Natta catalyst attributes
- Ionic initiator attributes
- User attributes

## Polymer Component Attributes

The polymer properties tracked as component attributes include:

- Segment fraction
- Segment flow
- Number-average degree of polymerization and molecular weight
- Weight-average degree of polymerization and molecular weight
- Z-average degree of polymerization and molecular weight
- Zeroth through third moment of chain length distribution
- Number of long and short chain branches
- Long and short chain branching frequency

There are component attributes available to track these properties for *dead polymer*, *live polymer*, and *aggregate polymer*. You may want to track information for live polymers for cases of free-radical polymerization where the *quasi-steady-state approximation* (QSSA) is not used. Site based component attributes are also available to accommodate multi-site type Ziegler-Natta catalyst polymerization. Composite. attributes are summed over all site types. They represent the average properties of the polymer.

*Polymer Attribute Sets*

In summary, there are six sets of polymer component attributes.

1. Composite Polymer Set contains the basic attributes which may be used for any type of polymerization, including the minimum required set for all simulation models.
2. Composite Live Polymer Set contains the attributes required to track the characteristics of live polymer chains in chain growth polymerization.
3. Composite Aggregate Polymer Set contains the attributes required to track the characteristics of aggregate polymer chain in ionic polymerization.
4. Site-Based Polymer Set contains attributes corresponding to the composite set, but structured to track information for each catalyst site type.
5. Site-Based Live Polymer Set contains attributes corresponding to the composite live polymer set, structured to track information by catalyst site type.
6. Site-Based Aggregate Polymer Set contains attributes corresponding to the composite aggregate polymer set, structured to track information by ionic site type.

Tables 2.5 through 2.10 list the component attributes available in each set. Attributes must be associated from these sets to each of your polymer components when building a simulation model. To simplify this, the attributes in the tables were grouped by model usage, or polymerization reaction type (e.g. physical property simulation model, free-radical polymerization model). Select a grouping and all the attributes needed will be retrieved automatically. Table 2.11 lists the minimum required attributes by model usage.

### *Table 2.5 Attribute Definitions - Composite Polymer Attribute Set*

| Name | Symbol† | Description | Equation‡ | Class | Dimension | Units |
|---|---|---|---|---|---|---|
| DPN | $DP_n$ | Number-average degree of polymerization | $DP_n = \lambda_1 / \lambda_0$ | 0 | 1 | Unitless |
| DPW | $DP_w$ | Weight-average degree of polymerization | $DP_w = \lambda_2 / \lambda_1$ | 0 | 1 | Unitless |
| DPZ | $DP_z$ | Z-average degree of polymerization | $DP_z = \lambda_3 / \lambda_2$ | 0 | 1 | Unitless |
| PDI | $PDI$ | Polydispersity index | $PDI = DP_w / DP_n$ | 0 | 1 | Unitless |
| MWN | $M_n$ | Number-average molecular weight | $M_n = DP_n \overline{M}_{seg}$ | 0 | 1 | Unitless |
| MWW | $M_w$ | Weight-average molecular weight | $M_w = DP_w \overline{M}_{seg}$ | 0 | 1 | Unitless |
| MWZ | $M_z$ | Z-average molecular weight | $M_z = DP_z \overline{M}_{seg}$ | 0 | 1 | Unitless |
| MWSEG | $\overline{M}_{seg}$ | Average segment molecular weight | $\overline{M}_{seg} = \sum F_p(i) M_i$ | 0 | 1 | Unitless |
| ZMOM | $\lambda_0$ | Zeroth moment of chain length distribution | ---- | 2 | 1 | Mole flow |
| FMOM | $\lambda_1$ | First moment of chain length distribution | $\lambda_1 = \sum \lambda_1(i)$ | 0 | 1 | Mole flow |
| SMOM | $\lambda_2$ | Second moment of chain length distribution | ---- | 2 | 1 | Mole flow |
| TMOM | $\lambda_3$ | Third moment of chain length distribution | ---- | 2 | 1 | Mole flow |
| SFLOW | $\lambda_1(i)$ | Mole flow of segments of type i | ---- | 2 | NSEG | Mole flow |
| SFRAC | $F_p(i)$ | Mole fraction of segments of type i | $F_p(i) = \lambda_1(i) / \lambda_1$ | 0 | NSEG | Unitless |
| EFRAC | $F_e(i)$ | Fraction of chain end segments of type i | $F_e(i) = \lambda_1(i) / \sum_{ends} \lambda_1(i)$ | 0 | NEND | Unitless |
| LCB | $LCB$ | Number of long chain branches | ---- | 2 | 1 | Mole flow |
| SCB | $SCB$ | Number of short chain branches | ---- | 2 | 1 | Mole flow |

† ***i = segment index***

***Moments of the chain length distribution are defined as follows:***

$$\lambda_m = \sum n^m Q_n$$

***Where:***

$m$ = ***0-3***

$n$ = ***chain length***

$Q_n$ = ***number of moles of polymer of length n.***

‡ ***Equation for recalculating class 0 attributes only. Class 2 attributes are integrated.***

*continued*

### *Table 2.5 Attribute Definitions - Composite Polymer Attribute Set (cont.)*

| Name | Symbol† | Description | Equation‡ | Class | Dimension | Units |
|---|---|---|---|---|---|---|
| FLCB | $FLCB$ | Long chain branching frequency | $FLCB = \frac{10^3 LCB}{\lambda_1}$ | 0 | 1 | Unitless |
| FSCB | $FSCB$ | Short chain branching frequency | $FSLB = \frac{10^3 SCB}{\lambda_1}$ | 0 | 1 | Unitless |
| PDV | $PD_v$ | Polydispersity for PSD (volume) | $PD_v = \frac{V_n}{V_v}$ | 0 | 1 | Unitless |
| PSDZMOM | $\nu_0$ | Zeroth moment of the particle size distribution (volume) | ---- | 2 | 1 | $\#/s$ |
| PSDFMOM | $\nu_1$ | First moment of the PSD (volume) | $\nu_1 = Mass / \rho$ | 0 | 1 | $m^3/s$ |
| PSDSMOM | $\nu_2$ | Second moment of the PSD (volume) | ---- | 2 | 1 | $m^6/s$ |
| PSDTMOM | $\nu_3$ | Third moment of the PSD (volume) | ---- | 2 | 1 | $m^9/s$ |
| VOLN | $V_n$ | Number average volume of the particles | $V_n = \frac{\nu_1}{\nu_0}$ | 0 | 1 | $m^3$ |
| VOLV | $V_v$ | Volume average volume of the particles | $V_v = \frac{\nu_2}{\nu_1}$ | 0 | 1 | $m^3$ |
| VOLZ | $V_z$ | Z-average volume of the particles | $V_z = \frac{\nu_3}{\nu_2}$ | 0 | 1 | $m^3$ |
| DIAV | $D_v$ | Volume average diameter | $D_v = 3\sqrt{\frac{6}{\pi}\frac{\nu_1}{\nu_0}}$ | 0 | 1 | $m$ |

† ***Moments of the chain length distribution are defined as follows:***

$$\lambda_m = \sum n^m Q_n$$

***Where:***

$m$ = ***0-3***

$n$ = ***chain length***

$Q_n$ = ***number of moles of polymer of length n.***

‡ ***Equation for recalculating class 0 attributes only. Class 2 attributes are integrated.***

### *Table 2.6 Attribute Definitions - Composite Live Polymer Attribute Set*

| Name | Symbol† | Description | Equation‡ | Class | Dimension | Units |
|---|---|---|---|---|---|---|
| LDPN | $DP_n^L$ | Number average DP of live polymer | $DP_n^L = \mu_1 / \mu_0$ | 0 | 1 | Unitless |
| LDPW | $DP_w^L$ | Weight average DP of live polymer | $DP_w^L = \mu_2 / \mu_1$ | 0 | 1 | Unitless |
| LPDI | $PDI^L$ | Polydispersity index of live polymer | $PDI^L = DP_w^L / DP_n^L$ | 0 | 1 | Unitless |
| LMWN | $M_n^L$ | Number average MW of live polymer | $M_n^L = DP_n^L M_{seg}^L$ | 0 | 1 | Unitless |
| LMWW | $M_w^L$ | Weight average MW of live polymer | $M_w^L = DP_w^L M_{seg}^L$ | 0 | 1 | Unitless |
| LMWSEG | $M_{seg}^L$ | Average segment molecular weight of live polymer | $M_{seg}^L = \sum LF_p(i) M_i$ | 0 | 1 | Unitless |
| LZMOM | $\mu_0$ | Zeroth moment of live polymer | $\mu_0 = \sum \mu_0(i)$ | 0 | 1 | Mole flow |
| LFMOM | $\mu_1$ | First moment of live polymer | $\mu_1 = \sum \mu_1(i)$ | 0 | 1 | Mole flow |
| LSMOM | $\mu_2$ | Second moment of live polymer | ---- | 2 | 1 | Mole flow |
| LSFLOW | $\mu_1(i)$ | Segment flow rates in live polymer | ---- | 2 | NSEG | Mole flow |
| LSFRAC | $LF_p(i)$ | Segment mole fraction in live polymer | $LF_p(i) = \mu_1(i) / \mu_1$ | 0 | NSEG | Unitless |
| LEFLOW | $\mu_0(i)$ | End segment flow rates in live polymer | ---- | 2 | NSEG | Mole flow |
| LEFRAC | $LF_e(i)$ | End segment mole fractions in live polymer | $LF_e(i) = \mu_0(i) / \mu_0$ | 0 | NSEG | Unitless |
| LPFRAC | $F_{lp}$ | Fraction of polymer that is live | $F_{lp} = \frac{\mu_0}{\lambda_0}$ | 0 | 1 | Mole fraction |

† ***i = segment index***

‡ ***Equation for recalculating class 0 attributes only. Class 2 attributes are integrated.***

### *Table 2.7 Attribute Definitions - Composite Aggregate Polymer Attribute Set*

| Name | Symbol† | Description | Equation‡ | Class | Dimension | Units |
|---|---|---|---|---|---|---|
| ADPN | $DP_n^A$ | Number average DP of aggregate polymer | $DP_n^A = \xi_1 / \xi_0$ | 0 | 1 | Unitless |
| ADPW | $DP_w^A$ | Weight average DP of aggregate polymer | $DP_w^A = \xi_2 / \xi_1$ | 0 | 1 | Unitless |
| APDI | $PDI^A$ | Polydispersity index of aggregate polymer | $PDI^A = DP_w^A / DP_n^A$ | 0 | 1 | Unitless |
| AMWN | $M_n^A$ | Number average MW of aggregate polymer | $M_n^A = DP_n^A M_{seg}^A$ | 0 | 1 | Unitless |
| AMWW | $M_w^A$ | Weight average MW of aggregate polymer | $M_w^A = DP_w^A M_{seg}^A$ | 0 | 1 | Unitless |
| AMWSEG | $M_{seg}^A$ | Average segment molecular weight of aggregate polymer | $M_{seg}^A = \sum AF_p(i) M_i$ | 0 | 1 | Unitless |
| AZMOM | $\xi_0$ | Zeroth moment of aggregate polymer | $\xi_0 = \sum \xi_0(i)$ | 0 | 1 | Mole flow |
| AFMOM | $\xi_1$ | First moment of aggregate polymer | $\xi_1 = \sum \xi_1(i)$ | 0 | 1 | Mole flow |
| ASMOM | $\xi_2$ | Second moment of aggregate polymer | $\xi_2 = \sum \xi_2(i)$ | 0 | 1 | Mole flow |
| ASFLOW | $\xi_1(i)$ | Segment flow rates in aggregate polymer | $\xi_1(i) = \sum \xi_1(i, j)$ | 0 | NSEG | Mole flow |
| ASFRAC | $AF_p(i)$ | Segment mole fraction in aggregate polymer | $AF_p(i) = \xi_1(i) / \xi_1$ | 0 | NSEG | Unitless |
| AEFLOW | $\xi_0(i)$ | End segment flow rates in aggregate polymer | $\xi_0(i) = \sum \xi_0(i, j)$ | 0 | NSEG | Mole flow |
| AEFRAC | $AF_e(i)$ | End segment mole fractions in aggregate polymer | $AF_e(i) = \xi_0(i) / \xi_0$ | 0 | NSEG | Unitless |
| APFRAC | $F_{ap}$ | Fraction of polymer that is aggregate | $F_{ap} = \frac{\xi_0}{\lambda_0}$ | 0 | 1 | Mole fraction |

† ***i = segment index***

***Equation for recalculating class 0 attributes only. Class 2 attributes are integrated.***

### *Table 2.8 Attribute Definitions - Site Based Polymer Attribute Set*

| Name | Symbol† | Description | Equation‡ | Class | Dimension | Units |
|---|---|---|---|---|---|---|
| SDPN | $DP_n(j)$ | Number average degree of polymerization at site j | $DP_n(j) = \lambda_1(j) / \lambda_0(j)$ | 0 | NSITE | Unitless |
| SDPW | $DP_w(j)$ | Weight average degree of polymerization at site j | $DP_w(j) = \lambda_2(j) / \lambda_1(j)$ | 0 | NSITE | Unitless |
| SDPZ | $DP_z(j)$ | Z-average degree of polymerization at site j | $DP_z(j) = \lambda_3(j) / \lambda_2(j)$ | 0 | NSITE | Unitless |
| SPDI | $PDI(j)$ | Polydispersity index at site j | $PDI(j) = DP_w(j) / DP_n(j)$ | 0 | NSITE | Unitless |
| SMWN | $M_n(j)$ | Number-average molecular weight at site j | $M_n(j) = DP_n(j)\overline{M}_{seg}(j)$ | 0 | NSITE | Unitless |
| SMWW | $M_w(j)$ | Weight-average molecular weight at site j | $M_w(j) = DP_w(j)\overline{M}_{seg}(j)$ | 0 | NSITE | Unitless |
| SMWZ | $M_z(j)$ | Z-average molecular weight at site j | $M_z(j) = DP_z(j)\overline{M}_{seg}(j)$ | 0 | NSITE | Unitless |
| SMWSEG | $\overline{M}_{seg}(j)$ | Average segment molecular weight at site j | $\overline{M}_{seg}(j) = \sum F_p(i,j)M_i$ | 0 | NSITE | Unitless |
| SZMOM | $\lambda_0(j)$ | Zeroth moment of chain length distribution at site j | ---- | 2 | NSITE | Mole flow |
| SFMOM | $\lambda_1(j)$ | First moment of chain length distribution at site j | $\lambda_1(j) = \sum \lambda_1(i,j)$ | 0 | NSITE | Mole flow |
| SSMOM | $\lambda_2(j)$ | Second moment of chain length distribution at site j | ---- | 2 | NSITE | Mole flow |
| STMOM | $\lambda_3(j)$ | Third moment of chain length distribution at site j | ---- | 2 | NSITE | Mole flow |
| SSFLOW | $\lambda_1(i,j)$ | Mole flow of segments of type i at site j | ---- | 2 | NSEG, NSITE | Mole flow |
| SSFRAC | $F_p(i,j)$ | Mole fraction of segments of type i at site j | $F_p(i,j) = \lambda_1(i,j) / \lambda_1(j)$ | 0 | NSEG; NSITE | Unitless |
| SEFRAC | $F_e(i,j)$ | Fraction of chain end segments of type i at site j | $F_e(i,j) = \lambda_1(i,j) / \sum_{ends} \lambda_1(i,j)$ | 0 | NEND, NSITE | Unitless |
| SLCB | $LCB(j)$ | Number of long chain branches at site j | ---- | 2 | NSITE | Mole flow |

† ***j = site number***

***i = segment index***

‡ ***Equation for recalculating class 0 attributes only. Class 2 attributes are integrated.***

*continued*

### *Table 2.8 Attribute Definitions - Site Based Polymer Attribute Set (cont.)*

| Name | Symbol† | Description | Equation‡ | Class | Dimension | Units |
|---|---|---|---|---|---|---|
| SSCB | $SCB(j)$ | Number of short chain branches at site j | ---- | 2 | NSITE | Mole flow |
| SFLCB | $FLCB(j)$ | Long chain branching frequency at site j | $FLCB(j) = \frac{10^3 LCB(j)}{\lambda_1(j)}$ | 0 | NSITE | Unitless |
| SFSCB | $FSCB(j)$ | Short chain branching frequency at site j | $FSLB(j) = \frac{10^3 SCB(j)}{\lambda_1(j)}$ | 0 | NSITE | Unitless |
| SPFRAC | $FSP(j)$ | Mass fraction of composite polymers at that site | $F_{sp}(j) = \frac{\lambda_0(j) M_{seg}(j)}{\sum \lambda_0(j) M_{seg}(j)}$ | 0 | NSITE | Unitless |

† ***j = site number***

***i = segment index***

‡ ***Equation for recalculating class 0 attributes only. Class 2 attributes are integrated.***

### *Table 2.9 Attribute Definitions - Site Based Live Polymer Attribute Set*

| Name | Symbol† | Description | Equation‡ | Class | Dimension | Units |
|---|---|---|---|---|---|---|
| LSDPN | $DP_n^L(j)$ | Number average DP of live polymer | $DP_n^L(j) = \mu_1(j) / \mu_0(j)$ | 0 | NSITE | Unitless |
| LSDPW | $DP_w^L(j)$ | Weight average DP of live polymer | $DP_w^L(j) = \mu_2(j) / \mu_1(j)$ | 0 | NSITE | Unitless |
| LSPDI | $PDI^L(j)$ | Polydispersity index of live polymer | $PDI^L(j) = DP_w^L(j) / DP_n^L(j)$ | 0 | NSITE | Unitless |
| LSMWN | $M_n^L(j)$ | Number average MW of live polymer | $M_n^L(j) = DP_n^L(j) M_{seg}^L(j)$ | 0 | NSITE | Unitless |
| LSMWW | $M_w^L(j)$ | Weight average MW of live polymer | $M_w^L(j) = DP_w^L(j) M_{seg}^L(j)$ | 0 | NSITE | Unitless |
| LSMWSEG | $M_{seg}^L(j)$ | Average segment molecular weight of live polymer | $M_{seg}^L(j) = \sum LF_p(i,j) M_i$ | 0 | NSITE | Unitless |
| LSZMOM | $\mu_0(j)$ | Zeroth moment of live polymer | $\mu_0(j) = \sum \mu_0(i,j)$ | 0 | NSITE | Mole flow |
| LSFMOM | $\mu_1(j)$ | First moment of live polymer | $\mu_1(j) = \sum \mu_1(i,j)$ | 0 | NSITE | Mole flow |
| LSSMOM | $\mu_2(j)$ | Second moment of live polymer | ---- | 2 | NSITE | Mole flow |
| LSSFLOW | $\mu_1(i,j)$ | Segment flow rates in live polymer | ---- | 2 | NSEG, NSITE | Mole flow |
| LSSFRAC | $LF_p(i)$ | Segment mole fraction in live polymer | $LF_p(i,j) = \mu_1(i,j) / \mu_1(j)$ | 0 | NSEG, NSITE | Unitless |
| LSEFLOW | $\mu_0(i,j)$ | End segment flow rates in live polymer | ---- | 2 | NSEG, NSITE | Mole flow |
| LSEFRAC | $LF_e(i,j)$ | End segment mole fractions in live polymer | $LF_e(i,j) = \mu_0(i,j) / \mu_0(j)$ | 0 | NSEG, NSITE | Unitless |
| LSPFRAC | $F_{lp}(j)$ | Fraction of polymer that is live | $F_{lp}(j) = \dfrac{\mu_0(j)}{\lambda_0(j)}$ | 0 | NSITE | Mole fraction |

† ***j = site number***

***i = segment index***

***Equation for recalculating class 0 attributes only. Class 2 attributes are integrated.***

### *Table 2.10 Attribute Definitions - Site Based Aggregate Polymer Attribute Set*

| Name | Symbol† | Description | Equation‡ | Class | Dimension | Units |
|---|---|---|---|---|---|---|
| ASDPN | $DP_n^A(j)$ | Number average DP of aggregate polymer | $DP_n^A(j) = \xi_1(j) / \xi_0(j)$ | 0 | NSITE | Unitless |
| ASDPW | $DP_w^A(j)$ | Weight average DP of aggregate polymer | $DP_w^A(j) = \xi_2(j) / \xi_1(j)$ | 0 | NSITE | Unitless |
| ASPDI | $PDI^A(j)$ | Polydispersity index of aggregate polymer | $PDI^A(j) = DP_w^A(j) / DP_n^A(j)$ | 0 | NSITE | Unitless |
| ASMWN | $M_n^A(j)$ | Number average MW of aggregate polymer | $M_n^A(j) = DP_n^A(j) M_{seg}^A(j)$ | 0 | NSITE | Unitless |
| ASMWW | $M_w^A(j)$ | Weight average MW of aggregate polymer | $M_w^A(j) = DP_w^A(j) M_{seg}^A(j)$ | 0 | NSITE | Unitless |
| ASMWSEG | $M_{seg}^A(j)$ | Average segment molecular weight of aggregate polymer | $M_{seg}^A(j) = \sum AF_p(i,j) M_i$ | 0 | NSITE | Unitless |
| ASZMOM | $\xi_0(j)$ | Zeroth moment of aggregate polymer | $\xi_0(j) = \sum \xi_0(i,j)$ | 0 | NSITE | Mole flow |
| ASFMOM | $\xi_1(j)$ | First moment of aggregate polymer | $\xi_1(j) = \sum \xi_1(i,j)$ | 0 | NSITE | Mole flow |
| ASSMOM | $\xi_2(j)$ | Second moment of aggregate polymer | ---- | 2 | NSITE | Mole flow |
| ASSFLOW | $\xi_1(i,j)$ | Segment flow rates in aggregate polymer | ---- | 2 | NSEG, NSITE | Mole flow |
| ASSFRAC | $AF_p(i)$ | Segment mole fraction in aggregate polymer | $AF_p(i,j) = \xi_1(i,j) / \xi_1(j)$ | 0 | NSEG, NSITE | Unitless |
| ASEFLOW | $\xi_0(i,j)$ | End segment flow rates in aggregate polymer | ---- | 2 | NSEG, NSITE | Mole flow |
| ASEFRAC | $AF_e(i,j)$ | End segment mole fractions in aggregate polymer | $AF_e(i,j) = \xi_0(i,j) / \xi_0(j)$ | 0 | NSEG, NSITE | Unitless |
| ASPFRAC | $F_{ap}(j)$ | Fraction of polymer that is aggregate | $F_{ap}(j) = \dfrac{\xi_0(j)}{\lambda_0(j)}$ | 0 | NSITE | Mole fraction |
| DSEFLOW | $\eta_0(i,j)$ | End segment flow rates in dissociated (from aggregate) polymer | ---- | 2 | NSEG, NSITE | --- |
| DSSFLOW | $\eta_1(i,j)$ | Segment polymer flow rates in dissociated (from aggregate) polymer | ---- | 2 | NSEG, NSITE | --- |
| DSSMOM | $\eta_2(j)$ | Second moment of dissociated (from aggregate) polymer | ---- | 2 | NSITE | --- |

† *j = site number*

*i = segment index*

‡ ***Equation for recalculating class 0 attributes only. Class 2 attributes are integrated.***

### *Table 2.11 Component Attribute Usage Summary*

| Model | Attributes |
|---|---|
| Property Models | MWN, DPN or both ZMOM and FMOM |
| | SFRAC or SFLOW |
| Emulsion | MWN, DPN or both ZMOM and FMOM |
| | SFRAC or SFLOW |
| | DIAV or both PSDZMOM and PSDFMOM |
| | Other polymer particle attributes (optional) |
| Free-Radical | MWN, DPN or both ZMOM and FMOM |
| | SFRAC or SFLOW |
| | Other composite attributes (optional) |
| | Composite live attributes (optional) |
| Step-Growth | MWN, DPN or both ZMOM and FMOM |
| | SFRAC or SFLOW |
| Ziegler-Natta | MWN, DPN or both ZMOM and FMOM |
| | SFRAC or SFLOW |
| | Other composite attributes (optional) |
| | Composite live attributes (optional) |
| | Site based component attributes (optional) |
| | Site based live component attributes (optional) |
| Ionic | SZMOM, LSEFLOW |
| | ASEFLOW, DSEFLOW (if association reaction present) |
| | LSSFLOW, SSFLOW |
| | ASSFLOW, DSSFLOW (if association reaction present) |

# Site-Based Species Attributes

## Ziegler-Natta Catalyst Attributes

Component attributes are used to track multi-site Ziegler-Natta catalyst site activity, in terms of mole flow and fraction of potential, inhibited, vacant, and dead sites. The occupied sites are not tracked since that information may be obtained from the live polymer zeroth moment of chain length distribution. The site types are defined as follows:

- Potential Sites - these are sites not yet activated.
- Vacant Site - these are activated sites without a growing polymer attached.
- Inhibited Sites - these are activated sites temporarily in an inactive state.
- Dead Sites - these are sites having permanently lost their catalytic activity.
- Occupied Sites - these are activated sites with a growing polymer attached.

Table 2.12 lists the catalyst component attributes.

***Table 2.12 Catalyst Component Attributes***

| Attribute | Description | Class | Dimension |
|---|---|---|---|
| CPSFLOW | Mole flow of potential sites | 2 | NSITE |
| CPSFRAC | Mole fraction of potential sites | 0 | NSITE |
| CVSFLOW | Mole flow of vacant sites of type k | 2 | NSITE |
| CVSFRAC | Mole fraction of vacant sites of type k | 0 | NSITE |
| CISFLOW | Mole flow of inhibited sites of type k | 2 | NSITE |
| CISFRAC | Mole fraction of inhibited sites of type k | 0 | NSITE |
| CDSFLOW | Mole flow of dead sites | 2 | NSITE |
| CDSFRAC | Mole fraction of dead sites | 0 | NSITE |

### Ionic Initiator Attributes

The component attributes are used to track various states of ionic initiator (free ions, ion pairs, dormant esters) using a multi-site model.

The three attributes are defined in Table 2.13 and described in detail in Section 4.5.

***Table 2.13 Ionic Component Attributes***

| Attribute | Description | | Class | Dimension |
|---|---|---|---|---|
| P0FLOW | Mole flow of | $P_0$ | 2 | NSITE |
| PT0FLOW | Mole flow of | $P_{T0}$ | 2 | NSITE |
| CIONFLOW | Mole flow of counter-ion | $C_I$ | 2 | NSITE |

## User Attributes

Generic component attributes are available for tracking user-specified data. These may be used to track additional properties not available through the pre-defined attributes.

User component attributes are available as Class 0 through Class 2 attributes. You must supply a Fortran subroutine to return rates of change for Class 2 attributes and recalculate Class 0 attributes. This would typically be a user kinetic routine. Table 2.14 lists the user component attributes available.

***Table 2.14 User Component Attributes***

| Attribute | Description | Dimension |
|---|---|---|
| CACLASS0 | Class 0 user attribute | 10 |
| CAUSR1…5 | Class 1 user attributes | 10 |
| CAUSRA…E | Class 2 user attributes | 10 |

# COMPONENT ATTRIBUTE INITIALIZATION

In cases where polymer is present in the process feed streams, values for the polymer component attributes must be specified. Enter this information while specifying the feed stream conditions.

Within Polymers Plus, material streams are made up of substreams which carry the flow of material of different types:

- Conventional vapor/liquid flow goes into the “Mixed” substream type
- Solid polymer and other solid components which do not participate in phase equilibrium go into the “Cisolid” substream type

Most simulations only make use of the “Mixed” substream. In this substream, you would enter the conditions, such as temperature and pressure, the number of phases (2 if both vapor and liquid are present), and the composition in terms of component flows or fractions (along with the total stream flow).

If one of the components for which you enter composition data is a polymer or a catalyst, you must specify its component attributes. Because users are allowed to specify either Class 0 or Class 2 component attributes, an initialization mechanism had to be defined to calculate the corresponding Class 2. Remember that the Class 2 attributes are the ones which are converged upon during simulation.

## Attribute Initialization Scheme

The attribute initialization scheme performs several important functions. In addition to calculating the needed Class 2 attributes, it automatically calculates an expanded component attribute set from the minimum required and specified by the user. The minimum required attributes are:

- Segment flow rates (SFLOW), or segment fractions (SFRAC)
- Number average degree of polymerization (DPN), or both
- Zeroth and first moment of chain length distribution (ZMOM and FMOM)

From this set, several other attributes can be calculated using the definitions given in Table 2.5 through 2.10. The scheme uses priority rules to decide how to calculate each attribute.

Table 2.15 describes the calculation methods and order of priority.

The initialization scheme is also used for recalculating Class 0 attributes during flowsheet convergence. Finally, it can be considered as a method of ensuring consistency between interrelated attributes.

### *Table 2.15 Polymers Plus Component Attribute Initialization Methodology*

| Attribute | Calculated from† | Priority |
|---|---|---|
| **Composite Bulk Polymer Attribute Set** | | |
| SFRAC | SFRAC | 1 |
| | SFLOW / SUM (SFLOW) | 2 |
| | 1 / NSEG | 3 |
| ZMOM | ZMOM | 1 |
| | FMOM / DPN | 2 |
| | FMOM*MWSEG / MWN | 3 |
| | PDI*FMOM*FMOM / SMOM | 4 |
| FMOM | SUM (SFLOW) | 1 |
| | PMASS / MWSEG | 2 |
| SMOM | SMOM | 1 |
| | FMOM*DPW | 2 |
| | FMOM*MWW / MWSEG | 3 |
| | FMOM*FMOM*PDI / ZMOM | 4 |
| | ZMOM | 5 |
| TMOM | TMOM | 1 |
| | SMOM*DPZ | 2 |
| | SMOM*MWZ / MWSEG | 3 |
| LCB | LCB | 1 |
| | FMOM*FLCB / 1.E3 | 2 |
| SCB | SCB | 1 |
| | FMOM*FSCB / 1.E3 | 2 |
| PSDZMOM | PSDZMOM | 1 |
| PSDFMOM | PSDFMOM | 1 |
| | PMASS / PDENS | 2 |
| PSDSMOM | PSDSMOM | 1 |
| PSDTMOM | PSDTMOM | 1 |
| VOLN | VOLN | 1 |
| | PSDFMOM / PSDZMOM | 2 |
| | 0.0 | 3 |
| VOLV | VOLV | 1 |
| | PSDSMOM / PSDSMOM / PSDFMOM | 2 |
| | 0.0 | 3 |
| VOLZ | VOLZ | 1 |
| | PSDTMOM / PSDSMOM | 2 |
| | 0.0 | 3 |
| DIAV | DIAV | 1 |
| | (6.0*PSDFMOM / $\pi$ / PSDZMOM) | 2 |
| | 0.0 | 3 |
| PDV | PDV | 1 |
| | (PSDZMOM*PSDSMOM) / (PSDFMOM) | 2 |
| | 0.0 | 3 |

*† PMASS is polymer mass, PDENS is polymer density*

*continued*

### *Table 2.15 Polymers Plus Component Attribute Initialization Methodology (cont.)*

| Attribute | Calculated from† | Priority |
|---|---|---|
| **Composite Live Polymer Attribute Set** | | |
| LSFRAC | LSFRAC | 1 |
| | LSFLOW / SUM (LSFLOW) | 2 |
| | 1 / NSEG | 3 |
| LZMOM | LZMOM | 1 |
| | LPFRA*ZMOM | 2 |
| | LFMOM / LDPN | 3 |
| | LFMOM*LMWSEG / LMWN | 4 |
| | LPDI*LFMOM*LFMOM / LSMOM | 5 |
| LFMOM | SUM (LSFLOW) | 1 |
| | LZMOM*LDPN | 2 |
| | LZMOM*LMWN / LMWSEG | 3 |
| | LZMOM*LSMOM / LPDI | 4 |
| LSMOM | LSMOM | 1 |
| | LFMOM*LDPW | 2 |
| | LFMOM*LMWW / LMWSEG | 3 |
| | LFMOM*LFMOM*LPDI / LZMOM | 4 |
| **Composite Aggregate PolymerAttribute Set** | | |
| ASFRAC | ASFRAC | 1 |
| | ASFLOW / SUM (ASFLOW) | 2 |
| | 1 / NSEG | 3 |
| AZMOM | AZMOM | 1 |
| | APFRA*ZMOM | 2 |
| | AFMOM / ADPN | 3 |
| | AFMOM*AMWSEG / AMWN | 4 |
| | APDI*AFMOM*AFMOM / ASMOM | 5 |
| AFMOM | SUM (ASFLOW) | 1 |
| | AZMOM*ADPN | 2 |
| | AZMOM*AMWN / AMWSEG | 3 |
| | AZMOM*ASMOM / APDI | 4 |
| ASMOM | ASMOM | 1 |
| | AFMOM*ADPW | 2 |
| | AFMOM*AMWW / AMWSEG | 3 |
| | AFMOM*AFMOM*APDI / AZMOM | 4 |

† ***PMASS is polymer mass, PDENS is polymer density***

*continued*

### *Table 2.15 Polymers Plus Component Attribute Initialization Methodology (cont.)*

| Attribute | Calculated from† | Priority |
|---|---|---|
| **Site Based Bulk Polymer Attribute Set** | | |
| SSFRAC | SSFRAC | 1 |
| | SSFLOW / SUM (SSFLOW) | 2 |
| | 1 / NSEG | 3 |
| SZMOM | SZMOM | 1 |
| | SFMOM / SDPN | 2 |
| | SFMOM*SMWSEG / SMWN | 3 |
| | SPDI*SFMOM*SFMOM / SSMOM | 4 |
| SFMOM | SUM(SSFLOW) | 1 |
| | SPFRAC*PMASS / SMWSEG | 2 |
| SSMOM | SSMOM | 1 |
| | SFMOM*SDPW | 2 |
| | SFMOM*SMWW / SMWSEG | 3 |
| | SFMOM*SFMOM*SPDI / SZMOM | 4 |
| | SZMOM | 5 |
| STMOM | STMOM | 1 |
| | SSMOM*SDPZ | 2 |
| | SSMOM*SMWZ / SMWSEG | 3 |
| SLCB | SLCB | 1 |
| | SFMOM*SFLCB / 1.E3 | 2 |
| SSCB | SSCB | 1 |
| | SFMOM*SFLCB / 1.E3 | 2 |
| **Site Based Live Polymer Attribute Set** | | |
| LSSFRAC | LSSFRAC | 1 |
| | LSSFLOW / SUM (LSSFLOW) | 2 |
| | 1 / NSEG | 3 |
| LSZMOM | LSZMOM | 1 |
| | LSPFRA*SZMOM | 2 |
| | LFSMOM / SLDPN | 3 |
| | LSFMOM*LSMWSEG / SLMWN | 4 |
| | LSPDI*LSFMOM*LSFMOM / LSSMOM | 5 |
| LSFMOM | SUM (LSSFLOW) | 1 |
| | LSZMOM*LSDPN | 2 |
| | LSZMOM*LSMWN / LSMWSEG | 3 |
| | DSQRT (LSZMOM*LSSMOM / LSPDI) | 4 |
| LSSMOM | LSSMOM | 1 |
| | LSFMOM*LSDPW | 2 |
| | LSFMOM*LSMWW / LSMWSEG | 3 |
| | LSFMOM*LSFMOM*LSPDI / LSZMOM | 4 |

† ***PMASS is polymer mass, PDENS is polymer density***

*continued*

### *Table 2.15 Polymers Plus Component Attribute Initialization Methodology (cont.)*

| Attribute | Calculated from† | Priority |
|---|---|---|
| **Site Based Aggregate Polymer Attribute Set** | | |
| ASSFRAC | ASSFRAC | 1 |
| | ASSFLOW / SUM (ASSFLOW) | 2 |
| | 1 / NSEG | 3 |
| ASZMOM | ASZMOM | 1 |
| | ASPFRA*SZMOM | 2 |
| | AFSMOM / SADPN | 3 |
| | ASFMOM*ASMWSEG / SAMWN | 4 |
| | ASPDI*ASFMOM*ASFMOM / ASSMOM | 5 |
| ASFMOM | SUM (ASSFLOW) | 1 |
| | ASZMOM*ASDPN | 2 |
| | ASZMOM*ASMWN / ASMWSEG | 3 |
| | DSQRT (ASZMOM*ASSMOM / ASPDI) | 4 |
| ASSMOM | ASSMOM | 1 |
| | ASFMOM*ASDPW | 2 |
| | ASFMOM*ASMWW / ASMWSEG | 3 |
| | ASFMOM*ASFMOM*ASPDI / ASZMOM | 4 |

† ***PMASS is polymer mass, PDENS is polymer density***

# SPECIFYING COMPONENT ATTRIBUTES

There are several categories of components for which you can specify component attributes:

- Polymers
- Site-based components
- Conventional components

## Specifying Polymer Component Attributes

See Specifying Polymers in Section 2.1.

## Specifying Site-Based Component Attributes

See Specifying Site-Based Components in Section 2.1.

## Specifying Conventional Component Attributes

You can associate attributes to conventional components. Typically you would select user attributes and would do this if you have a user subroutine to return values for these attributes.

To access the user component attribute selection form:

1. From the Data Browser, find the **Components** folder.
2. From the **Components** folder, go to **Attr-Comps**.

To associate user attributes to conventional components:

1. On the **Selection** tab sheet in the **Component** field specify the component name.
2. In the **Attribute** field specify the attribute name. Continue adding as many attributes as needed.

## Initializing Component Attributes in Streams or Blocks

If you have an attributed component present in a feed stream, you must specify component attribute values for that component.

To access the component attribute input form for a stream:

1. From the Process Flowsheet window, find the feed stream.
2. Right click on the feed stream and select **Input**.
3. From the stream input specifications sheet, scroll and click on the **Component Attr.** tab.
4. On the **Component Attr.** tab sheet, select the **Component ID**.
5. For each attribute, select the **Attribute ID.** enter the values for the attributes.

If you have an attributed component produced within a reactor, you can specify attribute values (product values or product value estimates) for that component. This is not available for all reactors.

See Section 5.1 for a description of the treatment of component attributes in reactors.

To access the component attribute input form for a reactor:

1. From the Process Flowsheet window, find the reactor.
2. Right click on the reactor and select **Input**.
3. From the reactor input specifications sheet, scroll and click on the **Component Attr.** tab.
4. On the **Component Attr.** tab sheet, select the **Component ID**.
5. For each attribute, select the **Attribute ID.** enter the values for the attributes.

# REFERENCES

Aspen Plus User Guide, Version 10, Aspen Technology, Inc. (1998).

# 2.3 STRUCTURAL PROPERTY DISTRIBUTIONS

This section discusses the mechanism available in Polymers Plus for tracking structural property distributions, in particular chain size distribution, for chain-growth polymerization processes.†

Topics covered include:

- Property Distribution Types
- Distribution Functions
- Distributions in Process Models
- Mechanism for Tracking Distributions
- Requesting Distribution Calculations

## PROPERTY DISTRIBUTION TYPES

The common polymer structural properties for which distributions are typically considered include:

- Chain size:  molecular weight or chain length
- Copolymer composition
- Degree of branching
- Polymer particle size

In order to accurately characterize a polymer component, and maintain control of polymer product properties, engineers must concern themselves with these distributions.

---

† Patent Pending Aspen Technology, Inc.

From a modeling standpoint, many theoretical and empirical functions have been developed to represent distributions. These functions tend to fall into categories derived from their formulation, or from their graphical representation.

For example, distributions which consider two dependent parameters simultaneously, e.g. chain size and copolymer composition, are termed *bivariate* distributions.

Distributions which mimic the normal bell-shaped graphical representation are called *unimodal* distributions.

This is in contrast with distributions which reveal several peaks and are called *bimodal* or *multimodal* distributions. Figure 2.2 shows examples of unimodal and bimodal distributions.

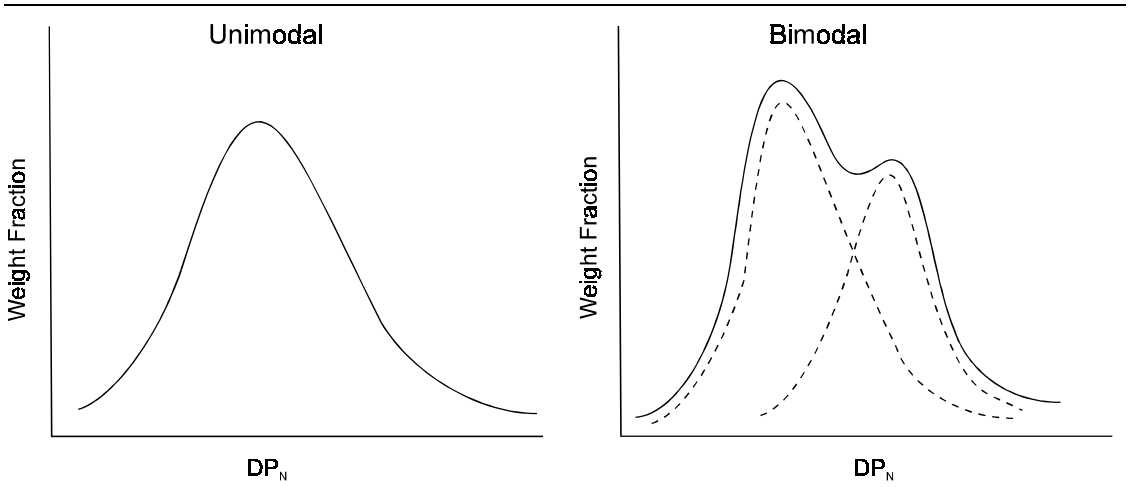


***Figure 2.2*** *Examples of Unimodal and Bimodal Distributions*

# DISTRIBUTION FUNCTIONS

In the majority of cases, the distribution functions proposed in the literature are based on a statistical approach and use one of three types of mathematical functions: binomial, Poisson or Gaussian.

The parameters in these distribution functions can easily be calculated from the polymer average properties (degree of polymerization, polydispersity index, etc.). The following are the common distribution functions which have been applied to the calculation of polymer property distributions:

- Schulz-Flory Most Probable (Flory, 1936/1953; Schulz, 1935/1939)
- Schulz (Schulz, 1935/1939)
- Weibull-Tung Generalized Exponential (Weibull, 1951; Tung, 1956)
- Normal (Biesenberger et al., 1983)
- Wesslau Logarithmic Normal (Wesslau, 1956)
- Lansing Logarithmic Normal (Lansing, 1935)
- Poisson (Biesenberger et al., 1983)
- Zimm (Zimm, 1948)
- Stockmayer Bivariate (Stockmayer, 1945)

In addition to these distribution functions, a method using the moments of distributions is also available (Tompa, 1976). Of these functions, two have greater importance for Polymers Plus.

## Schulz-Flory Most Probable Distribution

Schulz and Flory developed a one-parameter equation to represent the distribution of polymers falling into one of the following categories:

- Addition polymers - formed by a constant rate of initiation, with invariant monomer concentration, with termination by disproportionation only, and with no chain transfer to monomer
- Linear condensation polymers - obeying the assumption of equal reactivities of chain ends or linear condensation polymers formed by random interchange of units
- Low molecular weight polymer - formed from a high molecular weight polymer by random scission

The Schulz-Flory distribution is also known as the Most-Probable distribution since it is dictated by the probability of random events, such as the location of a scission reaction on a long-chain molecule. The number or mole-fraction distribution and the weight fraction distribution are given by:

*Mole-Fraction Distribution*

$$F(r) = p^{r-1}(1-p) \qquad \text{(number distribution)}$$

*Weight-Fraction Distribution*

$$W(r) = rp^{r-1}(1-p)^2 \qquad \text{(weight distribution)}$$

Where:

$p$ = extent of reaction

$r$ = size of the molecule or number of segments

For addition polymerizations $p$ is the probability that a growing live polymer molecule will propagate. For step-growth reactions, $p$ is the fractional conversion of monomer end groups.

From these distributions, the number, weight, and z average degree of polymerization are:

$$DP_n = \frac{1}{(1-p)}$$

$$DP_w = \frac{(1+p)}{(1-p)}$$

$$F(r) = p^{r-1}(1-p)$$

$$PDI = 1+p$$

To generate the distribution, $p$ can be calculated from degree of polymerization as:

$$p = 1 - \frac{1}{DP_n}$$

Note that the polydispersity approaches two as $p \rightarrow$ unity.

## Stockmayer Bivariate Distribution

There are cases where two polymer property distributions must be considered simultaneously, which are called bivariate. Stockmayer developed a distribution function to consider both chain size and composition distribution for example (Stockmayer, 1945).

This model may be extended to other combinations of polymer properties such as chain size and long chain branching distribution for the case of copolymers.

# DISTRIBUTIONS IN PROCESS MODELS

There is a great demand to know the full molecular weight distribution, particularly for complex distributions that may have a shoulder, or are even bimodal. This information is needed for optimization of rheological and mechanical properties of the final polymer product.

Within Polymers Plus a dual approach for determining polymer properties is used:

- *Method of moments* continues to be the preferred approach for calculating average properties.
- *Method of instantaneous properties* is used to calculate distributions. This method addresses the issue of data storage and computational complexity in tracking distributions.

Under special circumstances, the most general form of the instantaneous distribution function reduces to Flory's most probable distribution. The instantaneous distribution functions are unimodal. However, the distribution functions for polymer accumulated in a multi-reactor system may be multimodal.

## Average Properties and Moments

It is convenient to examine polymer molecular properties in terms of averages instead of considering the complete distribution. Average properties must be determined from the actual distributions either through *distribution moments* or through *instantaneous properties*.

During the discussion of polymer characterization properties in Section 2.2, the average properties tracked for polymers were described. These properties are calculated using the method of moments within kinetic models.

For a given property *s*, the property distribution may be described by a frequency function $f_s$ when the property is a discrete variable, and by a density function $f(s)$ when the property *s* is continuous.

Therefore, $f_s$ and $f(s)$ represent the portion (e.g. number, weight, volume, fraction) of the population whose property is exactly *s* (discrete) or whose property lies between *s* and *s + ds*.

The frequency and density distribution functions are respectively:

*Frequency Function*

$$F_S = \sum_{s_0}^{S} f_s$$

and

*Density Function*

$$F(S) = \int_{s_0}^{S} f(s)\, ds$$

Where:

$s_0$ = initial value of $s$

$S$ = arbitrary higher value (Biesenberger, 1983)

Distribution moments may be defined from the origin of the average property, i.e. property is equal to 0, or from the mean value of that property. The moments employed in Polymers Plus use the first approach.

In this case, the generalized form of the relationship between distribution moment and distribution function is shown below:

$$\mu_k \equiv \begin{cases} \sum_{all\ s} s^k f_s & \text{for the frequency function} \\ \int_{all\ s} s^k f(s)\, ds & \text{for the density function} \end{cases}$$

Where:

$\mu$ = moment

$k$ = moment order (e.g. 0-3 for zeroth through third moment)

$s$ = property value (e.g. chain length, molecular weight, particle size, etc.)

$f_s$ = frequency function

$f(s)$ = density function

*Average Properties*

The average properties can be calculated as ratios of the moments. Number average is the ratio of first to zeroth moment, $\mu_1 / \mu_0$. Weight or Volume average is the ratio of second to first moment, $\mu_2 / \mu_1$. Z-average is the ratio of third to second moment, $\mu_3 / \mu_2$.

For the case of chain length distribution the moment frequency distribution is given by:

$$\lambda_m = \sum n^m Q_n$$

Where:

$\lambda$ = moment

$m$ = moment order

$n$ = chain length or degree of polymerization

$Q_n$ = number of moles of polymer of length $n$

The average chain length properties are then:

$$DPn = \lambda_1 / \lambda_0$$

$$DPw = \lambda_2 / \lambda_1$$

$$DPz = \lambda_3 / \lambda_2$$

$$PDI = \lambda_2 \lambda_0 / \lambda_1^2$$

A similar definition of moments for the frequency distribution can be applied to molecular weight. Typically, in Polymers Plus it is applied to chain length. Then the average molecular weight values are determined using the average degree of polymerization and average segment molecular weight.

## Method of Instantaneous Properties

Applying the method of moments for the calculation of property distributions has several drawbacks. In addition to CPU requirements and computational complexity, a larger number of moments than currently calculated would be required. A knowledge of leading moments of a distribution does not permit one to unambiguously construct a complex distribution. One must therefore look beyond the method of moments for a more powerful method to predict these complex distributions.

A better approach for generating molecular weight distributions consists of storing reaction rate data throughout the kinetic calculations, and later using them to construct the full distribution of polymer accumulated in the reactor system. Such an approach was developed by Hamielec (Hamielec, 1992).

In the simplest case, linear polymerization in a single CSTR reactor, the ratios of termination and chain transfer reaction rates to propagation reaction rates are stored. The instantaneous chain length distribution is expressed as a function of these ratios and chain length.

For the case of two CSTRs in series, at steady-state, the outlet polymer distribution function is the weighted average of the distribution function in each CSTR taken separately. The case of a plug flow reactor can be approximated using multiple CSTRs, and similarly for a batch reactor.

By looking at the treatment of such reactor configurations, it can be deduced that the final polymer distribution is a result of the entire system of reactors. For this reason, the MWD implementation in Polymers Plus needs to consider the proper data structure to track distribution parameters at every point in the flowsheet. Users should be able to request MWD from any point in the flowsheet, and from this point the Aspen Plus flowsheet connectivity information can be used to track polymerization history.

The calculation of chain length distribution for a batch reactor from reaction rate parameters for linear addition polymerization was described by Hamielec (Hamielec, 1992).

Consider the equations for the generation and consumption of free radicals. A similar approach may be used for other active centers (Ziegler-Natta, metallocene, etc.):

*Radical Generation and Consumption Rates*

$$\left[R^o{}_l\right] = \frac{R_I + K_{fm}[M][R^o] + K_{fT}[T][R^o]}{K_p[M] + K_{fm}[M] + K_{fT}[T] + \left(K_{tc} + K_{td}\right)[R^o]} \quad \textbf{(2.1)}$$

$$\left[R^o{}_r\right] = \frac{K_p[M][R^o{}_{r-1}]}{K_p[M] + K_{fm}[M] + K_{fT}[T] + \left(K_{tc} + K_{td}\right)[R^o]} \quad \textbf{(2.2)}$$

Where:

$\left[R_I\right] = 2K_d f[I]$ = initiation rate

*Instantaneous Distribution Parameters*

Introducing two dimensionless parameters $\tau$ and $\beta$.

$$\tau = \frac{R_{td} + R_f}{R_p} = \frac{K_{td}[R^o] + K_{fm}[M] + K_{fT}[T]}{K_p[M]} \quad \textbf{(2.3)}$$

$$\beta = \frac{R_{tc}}{R_p} = \frac{K_{tc}[R^o]}{K_p[M]} \quad \textbf{(2.4)}$$

Where:

$R_p = K_p[R^o][M]$ = propagation rate

$R_{td} = K_{td}[R^o]^2$ = rate of termination by disproportionation

$R_{tc} = K_{tc}[R^o]^2$ = rate of termination by combination

$R_f = K_{fm}[R^o][M] + K_{fT}[R^o][T]$ = total rate of all chain transfer reactions

If we assume that the stationary-state hypothesis holds, then the initiation rate is equal to the sum of the termination rates, $R_I = R_{td} + R_{tc}$.

The equations for the rate of generation and consumption of radicals can be written as follows:

$$\left[R^o{}_l\right] = \frac{\tau + \beta}{1 + \tau + \beta}\left[R^o\right] \quad \textbf{(2.5)}$$

$$\left[R^o{}_r\right] = \frac{1}{1 + \tau + \beta}\left[R^o{}_{r-1}\right] \quad \textbf{(2.6)}$$

Therefore:

$$\left[R^o{}_r\right] = \left[R^o\right](\tau + \beta)\Phi^r \quad \textbf{(2.7)}$$

Where:

$$\Phi = \frac{1}{1+\tau+\beta} \quad \textbf{(2.8)}$$

The rate of production of polymer molecules of chain length $r$, $R_{Fp}(r)$ is given by:

$$R_{FP}(r) = \frac{1}{V}\frac{d\left(V\left[P_r\right]\right)}{dt} = \left(K_{fm}[M] + K_{fT}[T] + K_{td}\left[R^o\right]\right)\left[R^o{}_r\right] + \frac{1}{2}K_{tc}\sum_{s=1}^{r-1}\left[R^o{}_s\right]\left[R^o{}_{r-s}\right] \quad \textbf{(2.9)}$$

Substituting $[R_f^o]$ gives:

$$R_{FP}(r) = K_p\left[R^o\right][M](\tau+\beta)\left\{\tau + \frac{\beta}{2}(\tau+\beta)(r-1)\right\}\Phi^r \quad \textbf{(2.10)}$$

*Instantaneous Weight Chain Length Distribution*

Therefore, the instantaneous weight chain length distribution can be calculated from production rate of polymer molecules as follows:

$$W(r) = \frac{rR_{FP}(r)}{\sum_{r=1}^{\infty} rR_{FP}(r)} = \frac{(\tau+\beta)\left\{\tau + \frac{\beta}{2}(\tau+\beta)(r-1)\right\}r\Phi^r}{1+\tau+\beta} = (\tau+\beta)\left\{\tau + \frac{\beta}{2}(\tau+\beta)(r-1)\right\}r\Phi^{r+1} \quad \textbf{(2.11)}$$

In other words, *W*(*r*) is the weight chain length distribution of dead polymer chains produced in a small time interval *t* to *t*+*dt*, in a batch reactor. *W*(*r*) is also the weight chain length distribution of dead polymer chains produced in a CSTR operating at steady-state.

If $\beta << \tau$, which is the case when the polymer chains are formed by chain transfer or by termination by disproportionation, this equation reduces to:

$$W(r) = \tau^2 r\Phi^{r+1} = r\left(\frac{1}{1+\tau}\right)^{r-1}\left(\frac{\tau}{1+\tau}\right)^2 \quad \textbf{(2.12)}$$

Where:

$1/(1+\tau)$ = probability of growth for a polymer radical

$\tau/1+\tau$ = probability that a polymer radical stops growing

Since *r* is usually large, *W*(*r*) in Equation 2.11 can be approximated as a continuous function with small error:

$$W(r) \approx (\tau+\beta)\left\{\tau+\frac{\beta}{2}(\tau+\beta)(r-1)\right\} r.\exp\left\{-(\tau+\beta)r\right\} \quad \textbf{(2.13)}$$

For most free-radical polymerizations $(\tau+\beta) << 1$ and is of the order $10^{-6} - 10^{-2}$.

The weight-average chain length for polymer produced instantaneously is given by:

$$P_w = \sum_{r=1}^{\infty} rW(r) = \frac{\tau(2+\tau+\beta)+\beta(3+\tau+\beta)}{(\tau+\beta)^2} \approx \frac{2\tau+3\beta}{(\tau+\beta)^2} \quad \textbf{(2.14)}$$

The instantaneous number-average chain length distribution is given by:

$$Pn = \frac{1}{\sum_{r-1}^{\infty}\frac{W(r)}{r}} \frac{(1+\tau+\beta)}{\left(\tau+\beta/2\right)} \approx \frac{1}{\left(\tau+\beta/2\right)} \quad \textbf{(2.15)}$$

The polydispersity index for polymer produced instantaneously is given by:

$$PDI = \frac{P_w}{P_n} \approx \frac{(2\tau+3\beta)\left(\tau+\beta/2\right)}{(\tau+\beta)^2} \quad \textbf{(2.16)}$$

## Co-polymerization

Equation 2.13 applies to both homo- and co-polymerization with two or more monomer types. When chain growth polymerizations are done with active center types other than radicals (Ziegler-Natta, metallocene, etc.) $\beta = 0$ in Equation 2.13, and the instantaneous chain length distribution becomes a single parameter $\tau$ distribution, which is Flory's most probable distribution with a polydispersity index of 2.0.

Equation 2.13 is the main expression used in Polymers Plus to generate chain length distribution. Within the context of a polymerization reactor, this expression is valid for the case of linear chains of a homopolymer produced in a single CSTR at steady-state.

*Case of CSTR in Series*

For the case of two CSTRs in series, the end product polymer distribution is a composite which is a weighted average of the distributions of polymer produced in the first and the second reactor:

$$W_{out}(r) = \frac{m_1}{m} * W_1(r) + \frac{m_2}{m} * W_2(r) \quad \textbf{(2.17)}$$

Where:

$m = m_1 + m_2$ = total mass of polymer produced in the first and second reactor per unit time

The distribution function in each reactor is given by Equation 2.13 with the $\tau$ and $\beta$, varying from reactor 1 to reactor 2, and independent of time under steady-state operation.

*Plug Flow Reactor*

A plug flow reactor can be divided into several volume elements and treated as a series of CSTRs. The $\tau$, $\beta$, and polymer mass values are stored for each volume element and later used for the calculation of the composite chain length distribution function. A batch reactor is handled using a similar approach. In this case, the $\tau$, $\beta$, and polymer mass values are stored for each time element.

For linear chains of a copolymer, the difference from the homopolymer case can be factored into the calculation of the reaction rates for propagation, termination, and transfer reactions, $R_p$, $R_{tc}$, $R_{td}$, and $R_{fm}$.

# MECHANISM FOR TRACKING DISTRIBUTIONS

The method of instantaneous properties is used to generate chain length distributions in Polymers Plus. This method is applied at two levels:

- Reactor level for determining the distribution of polymer newly produced within the vessel (local distribution), and
- Flowstream level for determining the distribution of polymer produced up to that point in the flowsheet (cumulative distribution)

## Distributions in Kinetic Reactors

Within kinetic reactors, the method of instantaneous properties is used directly to determine the distribution of newly produced polymer. As kinetic calculations are being performed the values for the instantaneous properties $\tau$ and $\beta$, as calculated using Equations 2.3 and 2.4 respectively within the kinetic model, are saved for later calculation of the distribution. In addition, the polymer mass corresponding to these values is saved.

For a CSTR reactor, a single value of $\tau$ and $\beta$ is stored.

For a plug-flow or batch reactor, a value of $\tau$ and $\beta$ is stored at each profile point. In plug-flow reactors, the profile points represent equal-sized axial sections. In batch reactors, profile points are stored in fixed time intervals.

## Calculating Distribution of Polymer Produced

To calculate the distribution of polymer produced at the exit of the reactor, Equation 2.13 is applied to the calculated τ and β for the CSTR reactor. For the a plug-flow or batch reactor each profile element is represented as a CSTR for which that same equation is applied.

If the user selects the GPC distribution format the distribution is calculated as a function of log($r$) and the plot is generated as $rW(r)$ vs. $r$ with $r = 10^{\frac{(n*\log 10(DP_{\max}))}{No.\ Points-1}}$ where $n$ goes from 1 to number of requested distribution points.

To determine the distribution at the exit of these reactors, Equation 2.17 is applied to the total number of profile elements. The local distribution obtained is combined with distribution from the reactor inlet, where applicable and using Equation 2.17, then transferred through the outlet to downstream unit operations. The distribution is available to the user both as a data table and as a graphic plot.

## Multi-Site Kinetic Models

For multi-site kinetic models, such as the Ziegler-Natta model, an additional dimension is introduced. The τ and β parameters are stored for each site. Therefore the number of parameters for the case of a CSTR will be the user-specified total number of sites.

The distribution for each site is calculated using Equation 2.13, then Equation 2.17 is applied to calculate the composite polymer distribution. This procedure is applied once more to represent plug-flow and batch reactors as multiple CSTR reactors.

In any given reactor, the complete flowsheet connectivity is needed in order to calculate the cumulative distribution of the polymer. Each inlet stream has associated with it the distribution of accumulated polymer up to that point in the flowsheet.

## Distributions in Process Streams

The polymer distribution calculated within kinetic reactors is transferred into the outlet stream. This allows flowsheeting of the cumulative distribution data, i.e. the data follows the polymer component throughout the flowsheet. The cumulative distribution is stored within the stream.

Aspen Plus provides several different vehicles for associating data with process streams. These include:

- The basic stream vector which contains composition and state information
- The component attributes which are a fundamental tool in Polymers Plus
- Prop-Sets which allow users to request additional properties for streams
- Other non-accessible storage space

The first two categories are processed during convergence calculations while the last two are not.

The information used for calculating the distributions is derived from converged quantities. There is no need for applying convergence calculations to the distribution data itself. Therefore, the polymer distribution data is carried in non-accessible storage space.

Figure 2.3 illustrates the procedure followed to generate the distribution.

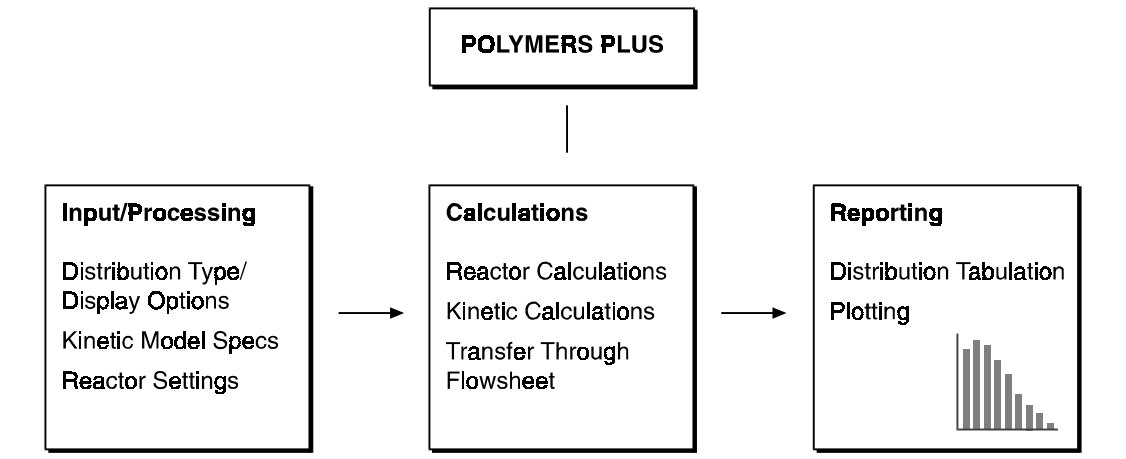


***Figure 2.3*** *Distribution Generation Procedure*

# REQUESTING DISTRIBUTION CALCULATIONS

In order to track distributions in your simulation, you must select the distribution characteristics. After the simulation is complete you must retrieve the distribution data for plotting. You can display and plot the distribution data for the polymerization reactor or you can display a distribution table for a stream or for the entire flowsheet.

## Selecting Distribution Characteristics

To access the Polymers Distributions specifications:

1. From the Data Browser, find the **Components** folder.
2. From the **Components** folder, go to **Polymers**.
3. From the **Polymers** folder, go to **Distributions**.
4. From the **Distributions** form, go to the **Selection** sheet.

To request tracking of distributions, from the Selection sheet:

1. In the **Polymer ID** field, select the polymer for which you would like distributions tracked.
2. In the **Distribution type** frame select the type of distribution.
3. Select the distribution plot characteristics: number of points for plot resolution, maximum for x-axis.
4. For a GPC distribution, select **Perform GPC Distribution Calculations**. The distribution will be calculated on a log scale as $rW(r)$ vs. $r$ where $r$ is number-average degree of polymerization.

## Displaying Distribution Data for a Reactor

Once simulation calculations are complete, you can display and plot the distribution data for the polymerization reactor (RCSTR, RPLUG, or RBATCH).

To display the distribution data for a polymerization reactor:

1. From the Process Flowsheet window, find the reactor.
2. Right click on the reactor and select **Results**.
3. From the reactor **Results** form, click on the **Distributions** tab.
4. On the **Distributions** tab sheet, select which distribution to view.

To plot the distribution data:

1. Select **Plot** on the main window menu bar.
2. From the Plot menu, select **Plot Wizard**.
3. Click on the **Next** button.
4. Click on a distribution plot sample, then click on **Next**.
5. Change the plot settings as desired, then click on **Next** or **Finish** to display the plot.
6. Click on the plot graphics to change the plot configuration as desired: reconfigure axes, legends, or change titles. If you requested the GPC distribution format, you must set the x-axis to a log scale for the plot to display properly.

## Displaying Distribution Data for Streams

To display a distribution data table for a stream:

1. From the Process Flowsheet window, find the feed stream.
2. Right click on the stream and select **Results**.
3. From the **Results** form, click on the **Poly. Curves** tab.
4. On the **Poly. Curves** tab sheet, select which distribution to view.

To display a distribution data table for the flowsheet:

1. From the Data Browser, find the **Results Summary** folder.
2. From the **Results Summary** folder, go to **Streams**.
3. From the **Streams** form, scroll to the right and locate the **Poly. Curves** tab.
4. On the **Poly. Curves** tab sheet, select which distribution to view.

To plot the distribution data:

1. Select **Plot** on the main window menu bar.
2. From the Plot menu, select **Plot Wizard**.
3. Click on the **Next** button.
4. Click on a distribution plot sample, then click on **Next**.
5. Change the plot settings as desired, then click on **Next** or **Finish** to display the plot.
6. Click on the plot graphics to change the plot configuration as desired: reconfigure axes, legends, or change titles.

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# 2.4 END-USE PROPERTIES

This section describes polymer end-use properties. First, an overview of the properties of interest for polymers is given, followed by methods available in Polymers Plus for calculating these properties.

Topics covered include:

- Polymer Properties
- End-Use Properties
- Method for Calculating End-Use Properties
- Calculating End-Use Properties

## POLYMER PROPERTIES

Polymer properties fall into many categories:

- Structural properties
- Thermophysical properties - which provide an indication of the thermodynamic behavior of polymers
- Thermochemical properties - which provide information on thermal stability
- Transport properties
- Processing and end-use properties - which provide information about processability and performance during end-use

Polymer structural properties do not provide a direct measure of the performance of the polymer product during processing or during its end use.

However, there is a relationship between polymer structural properties and the end use properties. For this reason, it is important to account for such properties within polymer process simulation models.

# END-USE PROPERTIES

The end-use or processing properties of interest for polymers include properties which describe their performance in the last stage of the polymer manufacturing process. Also of interest are properties relating to their performance when they reach the consumer.

Table 2.16 summarizes some end-use properties.

***Table 2.16 Some End-Use Properties***

| Category | Property | Availability in Polymers Plus |
|---|---|---|
| Processing | Melt index | Yes |
| | Melt index ratio (I10/I2) | No |
| | Moldability index | No |
| | Zero-shear viscosity | Yes |
| | Density of copolymer | Yes |
| Polymer product | Deformation | No |
| | Toughness/hardness | No |
| | Flammability | No |

## Relationship to Molecular Structure

The end-use properties such as rheological and mechanical properties are functions of the polymer structural properties and processing history. For example, long chain branching raises low shear viscosity, increases shear thinning, delays melt fracture, and increases extrudate swell.

For example, one could relate end-use properties of polyethylene to density, molecular weight, or melt index (Foster, 1993). See Table 2.17.

### *Table 2.17 Polyethylene End-Use Properties as Function of Molecular Weight, Melt Index, and Density*

| Properties | Molecular Weight ↑ | Melt Index ↑ | Density ↑ |
|---|---|---|---|
| Molecular weight | ↑ | ↓ | --- |
| Melt Index | ↓ | ↑ | --- |
| Impact strength | ↑ | ↓ | ↓ |
| Stress crack resistance | ↑ | ↓ | ↓ |
| Elongation | ↑ | ↓ | --- |
| Tensile strength | ↑ | ↓ | ↑ |
| Melt strength | ↑ | ↓ | --- |
| Orientation | ↑ | ↓ | --- |
| Elasticity | ↑ | ↓ | --- |
| Parision sag resistance | ↑ | ↓ | --- |
| Distortion resistance | ↓ | ↑ | --- |
| Weatherability | ↔ | ↔ | ↔ |
| Stiffness | --- | --- | ↑ |
| Heat Resistance | --- | --- | ↑ |
| Hardness | --- | --- | ↑ |
| Permeation resistance | --- | -- | ↑ |
| Shrinkage | --- | --- | ↑ |
| Creep resistance | --- | --- | ↑ |
| Transparency | --- | --- | ↓ |
| Flexibility | --- | --- | ↓ |

The basic structure-property relationship has attracted much research activity as the relationship is critical for product performance control. Readers are recommended to follow the recent developments in structure-property relationship (Bicerano, 1996; Foster, 1993).

# METHOD FOR CALCULATING END-USE PROPERTIES

Few end-use properties of interest for polymers are currently available in Polymers Plus. However, the method used for implementing the ones available is a good mechanism for users to incorporate additional ones if they have the necessary correlations to molecular structure and/or thermophysical properties.

Within Polymers Plus, end-use properties are available as property sets (Prop-Set). A Prop-Set provides a method for calculating properties for components within process flowstreams or vessel contents.

A number of built-in Prop-Sets are available (See your *Aspen Plus User Guide* documentation). In addition, Prop-Sets allow the specification of a property set with add-on user correlations. When doing this, a Fortran subroutine is required to perform the calculations.

End-use polymer properties are available as user property sets. This is because the correlations available to calculate these properties are highly empirical and are often dependent on the type of polymer for which they are used.

User property sets can easily be modified. Users can directly change the property correlation in the associated Fortran subroutine. Table 2.18 summarizes the Prop-Set name and Fortran subroutine name for the built-in user property sets.

### *Table 2.18 User Property Sets*

| Property | Prop-Set Name | Fortran Subroutine |
|---|---|---|
| Melt index | MI-KAR, MI-SIN | USRPRP |
| Intrinsic viscosity | IV | USRPRP |
| Zero-shear viscosity | ZVIS | USRPRP |
| Density of copolymer | DENS | USRPRP |

## Intrinsic Viscosity

The intrinsic viscosity is given as:

$$\eta = K\sqrt{M_w} + JM_w \qquad \textbf{(2.18)}$$

Where:

| | | |
|---|---|---|
| $\eta$ | = | intrinsic viscosity |
| $M_w$ | = | weight-average molecular weight |
| $J$ and $K$ | = | correlation constants |

## Zero-Shear Viscosity

For some ethyl branched paraffinic monodisperse polymers, Arnett and Thomas reported an empirical correlation for zero-shear viscosity as a function of molecular weight, number of branched sites per 1000 carbon atoms, and temperature (Arnett and Thomas, 1980).

$$\ln \eta_0 = a \ln M_w + \frac{d(1+cn)^3}{T} e^{bn} + B(n) \qquad \textbf{(2.19)}$$

Where:

| | | |
|---|---|---|
| $\eta_0$ | = | zero shear viscosity in Poise |
| $M_w$ | = | molecular weight |
| $n$ | = | number of branched sites per 1000 carbon atoms |
| $a$ | = | 3.41 |
| $d$ | = | 3523 |
| $c$ | = | 0.832 |
| $b$ | = | 2.368 |
| $B(n)$ | = | function of number of branches with: |
| $B(0)$ | = | -35.78 |
| $B(0.02)$ | = | -37.04 |
| $B(0.069)$ | = | -38.11 |
| $B(0.13)$ | = | -40.88 |
| $B(0.183)$ | = | -43.54 |

## Density of Copolymer

Randall and Ruff presented an empirical correlation for semicrystalline copolymer density (Randall and Ruff, 1988).

$$\frac{\rho - \rho_a}{\rho_c - \rho_a} = a + b\left(1-\gamma\right)^2 \sum_{i=1}^{n} i\gamma^i \qquad \textbf{(2.20)}$$

Where:

$\rho$ = actual density
$\rho_c$ = crystalline density
$\rho_a$ = amorphous density
$a$ and $b$ = correlation constants
$n$ = minimum crystallization run length of monomer
$\gamma$ = reaction probability that monomer is followed by similar monomer

## Melt Index

Karol and colleagues suggested a Quackenbos equation for high density polyethylene prepared with chromocene-based catalysts (Karol, et al, 1973; Quackenbos, 1969):

$$MI = a\left(bM_w + cM_n\right)^d \qquad \textbf{(2.21)}$$

Where:

$MI$ = melt index
$a$ = $1.0 \times 10^{18}$
$b$ = 0.2
$c$ = 0.8
$d$ = -3.9
$M_w$ = weight-average molecular weight
$M_n$ = number-average molecular weight

Sinclair suggested a simpler correlation (Sinclair, 1983):

$$MI = \left(\frac{a}{M_w}\right)^{\frac{1}{b}} \qquad \textbf{(2.22)}$$

Where:

$a$ = 111,525
$b$ = 0.288

## Melt Index Ratio

The Quackenbos equation can also be used to correlate melt index ratio.

# CALCULATING END-USE PROPERTIES

End-use properties are calculated as Prop-Sets. You must first select which end-use property to include in the simulation, then you must define this property as a Prop-Set.

## Selecting an End-Use Property

To access end-use property Prop-Sets:

1. From the Data Browser, find the **Properties** folder.
2. From the **Properties** folder, go to **Advanced**.
3. From the **Advanced** folder, select **User Properties**.
4. From the **User Properties** object manager, select **New**.

   If necessary, change the default ID for the user-property and click on **OK**.
5. From the User Properties **Specifications** tab sheet, choose the standard property as the type (default), then provide the subroutine name.

Create one User-Property for each end-use property.

## Adding an End-Use Property Prop-Set

To access Prop-Sets:

1. From the Data Browser, find the **Properties** folder.
2. From the **Properties** folder, go to **Prop-Sets**.
3. From the **Prop-Sets** object manager, select **New**.

   If necessary, change the default ID for the Prop-set and click on **OK**.
4. From the Prop-Set **Properties** tab sheet, in the **Physical Properties** field, select the ID for the end-use property User-Property.

   You can have as many User-Properties as desired.

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# 3 THERMODYNAMIC PROPERTIES

This chapter discusses thermodynamic properties of polymer systems. The importance of these properties in process modeling is summarized. The differences between thermodynamic properties of polymers and those of small molecules are outlined.

Topics covered include:

- Properties of Interest in Process Simulation
- Differences Between Polymers and Non-polymers
- Modeling Phase Equilibria in Polymer - Containing Mixtures
- Modeling Other Thermophysical Properties of Polymers
- Property Models Available in Polymers Plus
- Property Methods
- Thermodynamic Data for Polymers

Following this introduction, separate sections are devoted to the models available.


| SECTIONS | PAGE |
|---|---|
| 3.1 Van Krevelen Property Models | (3•21) |
| 3.2 Tait Molar Volume Model | (3•51) |
| 3.3 Polymer Viscosity Models | (3•55) |
| 3.4 Flory-Huggins Activity Coefficient Model | (3•73) |
| 3.5 NRTL Activity Coefficient Models | (3•79) |
| 3.6 UNIFAC Activity Coefficient Model | (3•89) |
| 3.7 Polymer UNIFAC Free Volume Model | (3•95) |
| 3.8 Polymer Ideal Gas Property Model | (3•99) |
| 3.9 Sanchez-Lacombe EOS Model | (3•105) |
| 3.10 Polymer SRK EOS Model | (3•115) |
| 3.11 SAFT EOS Model | (3•123) |

# PROPERTIES OF INTEREST IN PROCESS SIMULATION

Steady-state or dynamic process simulation is in most instances a form of performing simultaneous mass and energy balances. Rigorous modeling of mass and energy balances requires the calculation of *phase* and *chemical equilibria* and other *thermophysical properties*. In addition to the steps governed by equilibrium, there are rate-limited chemical reactions, and mass and heat transfer limited unit operations in a given process. Therefore, a fundamental understanding of the *reaction kinetics* and *transport phenomena* involved is a prerequisite for its modeling.

In process modeling, in addition to the properties needed for performing mass and energy balances and evaluating time dependent characteristics, detailed equipment design requires the calculation of additional thermophysical properties for equipment sizing. For detailed discussion of all these issues, the reader is referred to excellent references available in literature (Bicerano, 1993; Prausnitz et al., 1986; Reid et al., 1987; Sandler, 1988, 1994; Van Krevelen, 1990; Van Ness, 1964; Walas, 1985).

## Properties for Equilibrium, Mass and Energy Balances

Often chemical and phase equilibria play the most fundamental role in mass and energy balance calculations. There are two ways of calculating chemical and phase equilibria. The classical route is to evaluate *fugacities* or *activities* of the components in the different phases, and find, at given conditions, the compositions that obey the equilibrium requirement of equality of fugacities for all components in all phases.

Fugacities or activities are quantities related to Gibbs energy, and often it is more convenient to evaluate a *fugacity coefficient* or an *activity coefficient* rather than the fugacity and activity directly. Details on the calculation of these quantities are in *Aspen Plus Physical Property Methods and Models*.

Another method of calculating chemical and phase equilibria consists of searching for the minimum total of the mixture Gibbs energies for the different phases involved. This is the *Gibbs energy minimization*. This technique can be used to calculate simultaneous phase and chemical equilibria. Gibbs energy minimization is discussed in *Aspen Plus Physical Property Methods and Models*.

In performing energy balances, the interest is in changes in the energy content of a system, a section of a plant or a single unit, in a process. Depending upon the nature of the system, either an *enthalpy* (usually for flow systems such as heat exchangers, flash towers in which pressure changes are modest) or an *internal energy* (for systems such as closed batch reactors) balance is performed. These balances are often expressed as heat duty of a unit, yet the data on substances are usually measured as *constant pressure heat capacity* $(\partial H / \partial T)_P$, or as *constant volume heat capacity* $(\partial U/\partial T)_V$. Consequently, it is necessary to calculate temperature derivatives of enthalpy and internal energy.

## Properties for Detailed Equipment Design

Mixture *density* is required for equipment sizing. For the calculation of efficiency of pumps and turbines, *entropy* is needed. Entropy is usually derived from enthalpy and *Gibbs energy*. For detailed heat-exchanger design, *viscosity* and *thermal conductivity* of the mixture are needed. In detailed rating or design of column trays or packing, *surface tension* may be needed in addition to viscosity. Finally, in the calculation of mass transfer rates, *diffusion coefficient* is used.

## Summary of Important Properties for Modeling

The most important properties for process simulation are therefore:

| **Thermodynamic properties** | **Transport properties** |
|---|---|
| Fugacity (or thermodynamic potential) | Viscosity |
| Gibbs energy | Thermal conductivity |
| Internal energy, or $C_V$ | Surface tension |
| Enthalpy, or $C_P$ | Diffusivity |
| Entropy | |
| Density | |

# DIFFERENCES BETWEEN POLYMERS AND NON-POLYMERS

The word polymer derives from the Greek words *poly* ≡ many and *meros* ≡ part. A polymer consists of a large number of segments (repeating units of identical structure). Because of their structure, polymers exhibit thermodynamic properties significantly different than those of standard molecules (solvents, monomers, other additive solutes), consequently different property models are required to describe their behavior. For example, polymers being orders of magnitude larger molecules, have substantially more spatial conformations than the small molecules. This affects equilibrium properties such as the entropy of mixing, as well as non-equilibrium properties like viscosity. Unlike conventional molecules, polar interactions (between dipoles, quadrupoles etc., also called London-van-der-Waals or dispersion forces) among the segments of a single molecule play a role in thermodynamic behavior of polymers and their mixtures. Moreover, when polymer molecules interact with conventional small molecules, due to their large size, only a fraction of segments of the polymer molecule may be involved rather than the whole molecule. All these segment-segment and segment-conventional molecule interactions are influenced by the spatial conformations mentioned above.

Besides the different spatial conformations a single polymer molecule can have, they also exhibit chain length distributions, isomerism for each chain length due to branching distributions of co-monomer composition, and stereo chemical configuration of segments in a chain.

Detailed discussion of these issues are beyond the scope of this document, the reader is referred to excellent sources available in literature for this purpose (Brandup and Immergut, 1975; Cotterman and Prausnitz, 1991; Folie and Radosz, 1995; Kroschwitz, 1990; Sanchez, 1992; Van Krevelen, 1990; Bicerano 1993; Fried, 1995; Ko et al, 1991). A simplified overview is presented here from a modeling point of view.

*Polymer Polydispersity*

When modeling polymer phase equilibrium, one must take into account the basic polymer characteristics briefly mentioned above. First, no polymer is 'pure'. Rather, a polymer is a mixture of components with differing chain length, chain composition, and degree of branching. In other words, polymers are polydisperse. For the purposes of property calculations, this makes a polymer a mixture of an almost infinite number of components. In the calculation of phase equilibria of polymer solutions, some physical properties of the solution, such as vapor pressure depression, can be related to average polymer structure properties. On the other hand, physical properties of the polymer itself, for example distribution of the polymer over different phases or fractionation, can not be related to the average polymer structure properties. It is also impossible to take each individual component into account, therefore, compromise approximations are made to incorporate information about *polydispersity* in polymer process modeling.

Long-chain polymers have very low vapor pressures and are considered nonvolatile. Short-chain polymers may be volatile, these species can be treated as oligomers as discussed later in this section. Nonvolatile nature of polymers must be taken into account in developing models to describe polymer phase behavior, or when a model developed for conventional molecules is extended for use with polymers. Polymers can not exhibit a critical point either, since they decompose before they reach their critical temperatures.

In the pure condensed phase, polymers are either a liquid-like *melt*, *amorphous solid*, or a *semi-crystalline solid* Due to their possible semi-crystalline nature in the solid state, polymeric materials may exhibit two major types of transition temperatures from solid to liquid. A completely amorphous solid is characterized by *glass transition temperature*, $T_g$ at which it turns into melt from amorphous solid.

A *semi-crystalline* polymer is not completely crystalline, but still contains unordered amorphous regions in its structure. Such a polymer, upon heating, exhibits both a $T_g$, and a *melting temperature* $T_m$, at which phase transition of crystalline portion of the polymer to melt occurs. Thus, a semi-crystalline polymer may be treated as a glassy solid at temperatures below $T_g$, a rubbery solid between $T_g$ and $T_m$, and a melt above $T_m$.

The knowledge of state of aggregation of polymer in the condensed phase is important because all thermophysical characteristics change from one condensed state to another. For example, monomers and solvents are soluble in melt and in amorphous solid polymer, but crystalline areas are inert and do not participate in phase equilibrium. Other thermodynamic properties such as heat capacity, density etc. are also significantly different in each phase.

Another very important characteristic of the polymers is their *viscoelastic* nature that affects their transport properties enormously. The models to characterize viscosity of polymers or diffusion of other molecules in polymers must therefore be unique.

*Oligomers*

In process modeling, we also deal with *oligomers.* An oligomer is a substance that contains only a few monomeric segments in its structure, and its thermophysical properties are somewhere between a conventional molecule and a polymer. They can be considered like a heavy hydrocarbon molecule, and act like one. In most cases they can be simulated as a heavy conventional molecule. Polymers Plus permits the user to define a substance as oligomer, apart from standard molecules and polymers.

# MODELING PHASE EQUILIBRIA IN POLYMER - CONTAINING MIXTURES

In modeling phase equilibrium of polymer mixtures, there are two broad categories of problems that are particularly important. The first is the solubility of monomers, other conventional molecules used as additives, and solvents in a condensed phase containing polymers, and the second is the phase equilibrium when two polymer-containing condensed phases are in coexistence.

*VLE in Polymer Solutions*

A good example of the first case is the *devolatilization* of monomers, solvents and other conventional additives from a polymer. The issue here is to determine the extent of solubility of conventional molecules in the polymer at a given temperature and a pressure. The polymer may be a melt, an amorphous solid, or a semi-crystalline solid.

An amorphous polymer is treated as a pseudo-liquid. If the polymer is semi-crystalline, then one would compute overall solubility based on the solubility in the amorphous polymer and the fraction of amorphous polymer in the total polymer phase.

This problem is somewhat similar to a *vapor-liquid equilibrium (VLE)* of conventional systems. The thermodynamic model selected can be tested by investigating pressure-composition phase diagrams of polymer-solvent pairs at constant temperature. An example is shown in Figure 3.1.

Usually a flash algorithm is used to model the devolatilization process. Proven vapor-liquid equilibrium flash algorithms have been widely used for polymer systems. In these flash algorithms calculations can be done with a number of options such as temperature and pressure specified, temperature and vapor fraction (dew point or bubble point) specified, pressure and vapor fraction specified, pressure and heat duty specified, and vapor fraction and heat duty specified. It is important to stress that in such calculations polymers are considered nonvolatile while solvents, monomers and oligomers are distributed between vapor and liquid phases.

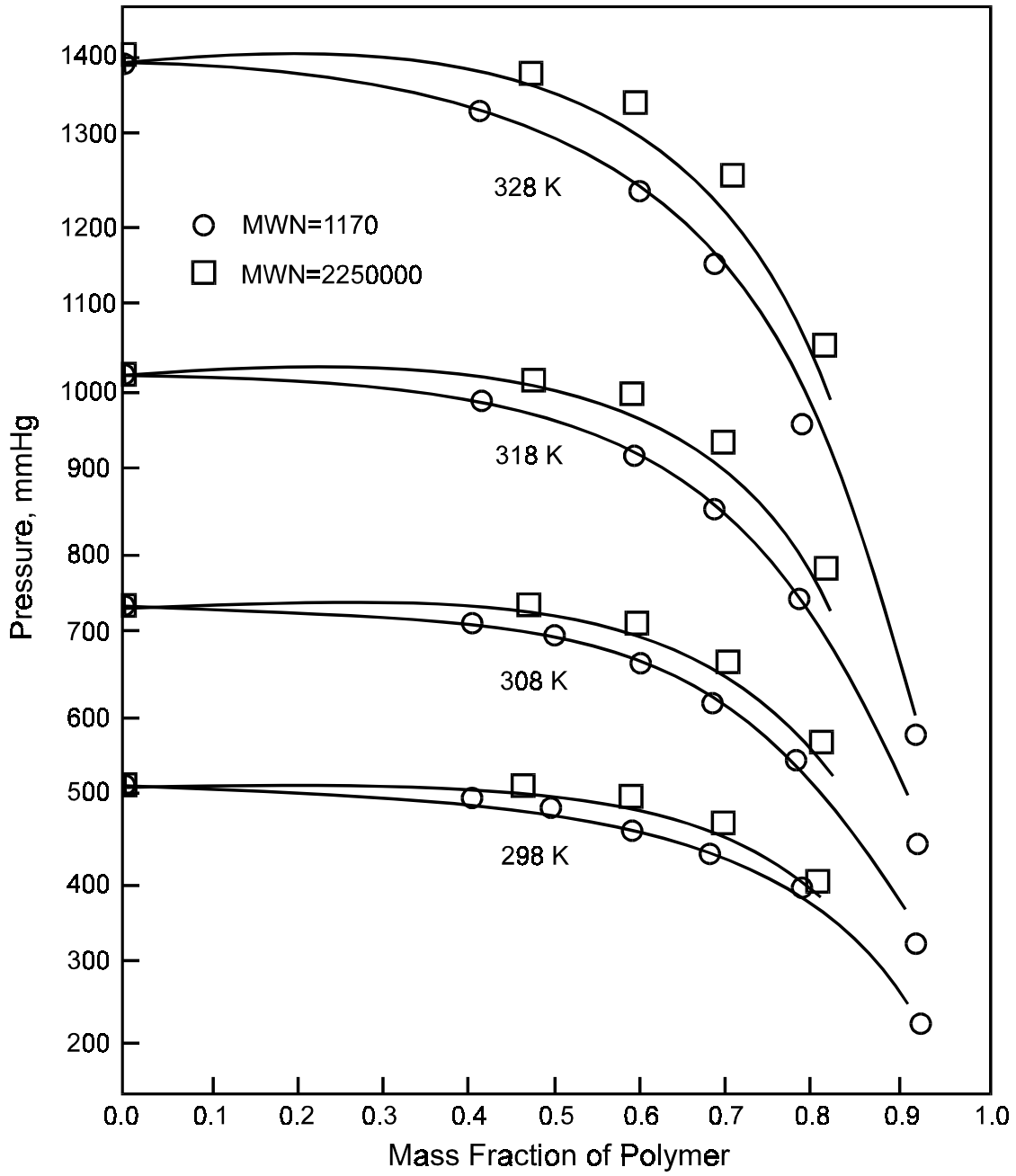


***Figure 3.1*** *PIB-N-Pentane Binary System (Data from compilation of Wohlfarth, 1994)*

Another example in this category is modeling of a polymerization reaction carried out in a liquid solvent with monomer coming from the gas phase. It is important to know the solubility of the monomer gas in the reaction solution, as this quantity directly controls the polymerization reaction kinetics in the liquid phase. In such a case, the mixture may contain molecules of a conventional solvent, dissolved monomer, other additive molecules, and the polymer either as dissolved in solution or as a separate particle phase swollen with solvent, monomer and additive molecules. Interactions of various conventional molecules in the solution with the co-existing polymer molecules have direct effect on the solubility of the monomer gas in the solution. Again, the phase equilibrium problem can be considered as a VLE (polymer dissolved in solution) or as a vapor-liquid-liquid equilibrium (VLLE; polymer in a separate phase swollen with conventional molecules).

*LLE in Polymer Solutions*

*Liquid-liquid phase equilibrium (LLE)* between two polymer containing phases is also important in modeling polymer processes. The overall thermodynamic behavior of two co-existing liquid phases is shown in Figure 3.2. In the figure, the space under the saddle is the region where liquid-liquid phase split occurs. Above that region, only a single homogeneous fluid phase exists. Various two-dimensional temperature-composition projections are also shown in the figure. In these projections several phase behavior types common in polymer-solvent systems are indicated. For example, at certain pressures, polymer-solvent mixtures exhibit two distinctly different regions of immiscibility.

These regions are characterized by the *upper critical solution temperature (UCST)* and the *lower critical solution temperature (LCST)*. UCST characterizes the temperature below which a homogeneous liquid mixture splits into two distinct phases of different composition. This phase behavior is rather common, and it is observed in many kinds of mixtures of conventional molecules and polymers. LCST represents the temperature above which a formerly homogeneous liquid mixture splits into two separate liquid phases. This thermally induced phase separation phenomenon is observed in mixtures of conventional molecules only when strong polar interactions exist (such as aqueous solutions). However, for polymer-solvent mixtures the existence of a LCST is the rule, not the exception (Sanchez, 1992).

In polymerization processes, especially those carried out at high pressures in the gas phase, such as LDPE production, it is important to estimate the boundaries of these regions of immiscibility. It is directly pertinent to modeling of reaction kinetics whether the reactive mixture remains a homogeneous fluid phase or splits into two liquid phases.

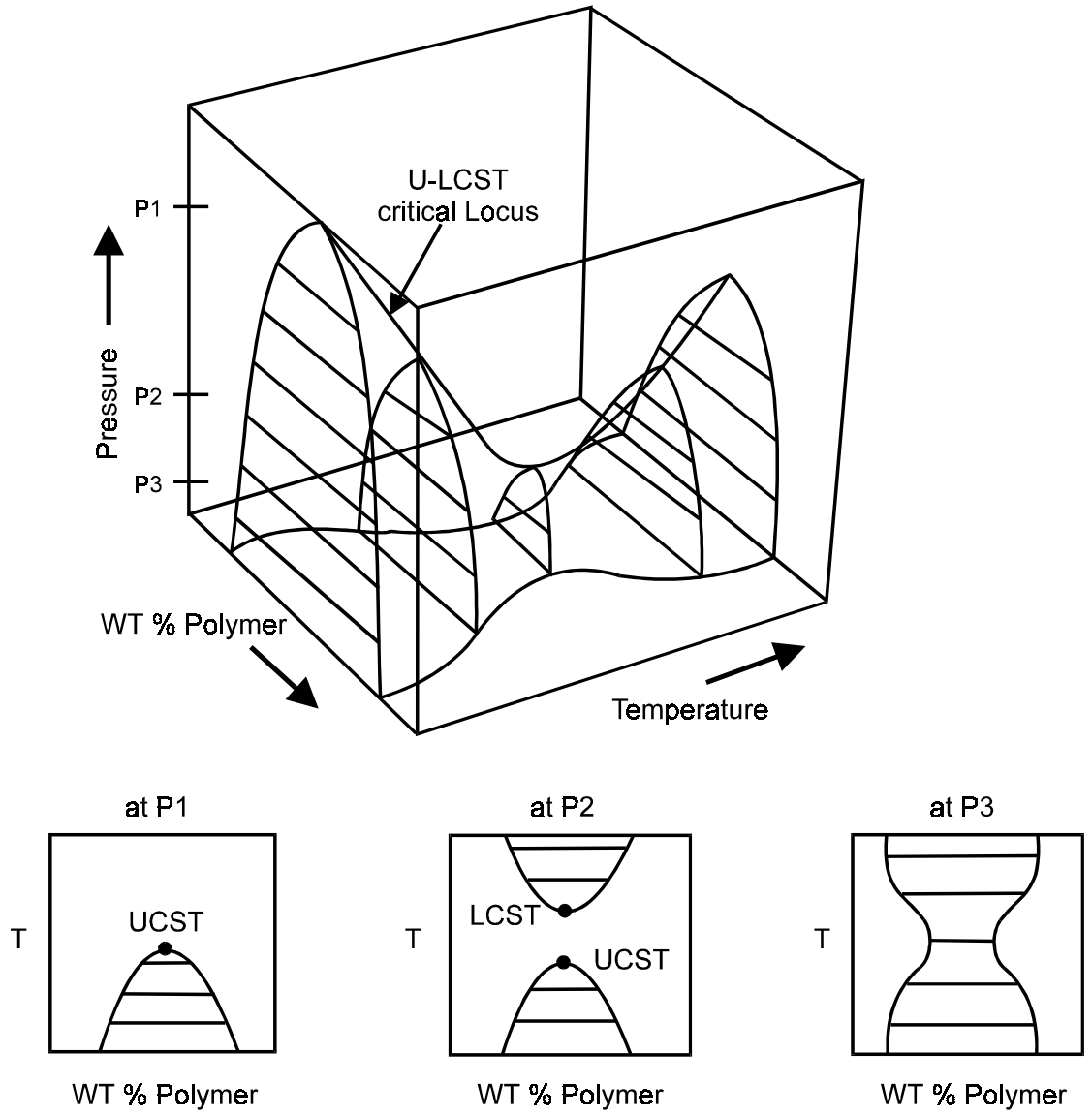


***Figure 3.2*** *LCST-UCST Behavior of Polymer Mixtures (Folie and Radosz, 1995)*

*Polymer Fractionation*

Another process where LLE behavior plays a role is *polymer fractionation*. A classical method of fractionating a polydisperse polymer is to dissolve the polymer completely in a 'good' solvent and then progressively add small amounts of a poor solvent (or antisolvent). Upon addition of the antisolvent, a second phase primarily consisting of lowest-molecular weight polymers will form. The system can be modeled as a LLE system.

Existing liquid-liquid equilibrium and vapor-liquid-liquid equilibrium flash algorithms can not be applied to solve these LLE systems with nonvolatile polymers, unless they are considered as oligomers with 'some' volatility.

These flash algorithms are based on solving a set of nonlinear algebraic equations derived from the isofugacity relationship for each individual component. Such an isofugacity relationship can not be mathematically established for nonvolatile polymer components. In such cases, the use of the Gibbs free energy minimization technique usually offers a more robust way of estimating the number of existing phases and their compositions..

# MODELING OTHER THERMOPHYSICAL PROPERTIES OF POLYMERS

Correlations for other important thermophysical properties of pure polymers such as heat capacity, density, viscosity are essentially empirical in nature. Van Krevelen developed an excellent group contribution methodology to predict a wide variety of thermophysical properties for polymers, using polymer molecular structure, in terms of functional groups, and polymer compositions (Van Krevelen, 1990). These relations are basically applicable to random linear copolymers.

Group contribution techniques can not be applied to polymers containing exotic structural units, if no experimental data is available for estimating contributions for functional groups not studied previously. To overcome these limitations, Bicerano developed a new generation of empirical quantitative structure-property relationships in terms of topological variables (Bicerano, 1993).

Correlations for predicting thermophysical properties of polymer mixtures are not well established. Typically, pure component properties are first estimated for polymers, monomers, and solvents by various techniques. Properties of polymer solutions are then calculated with mass fraction or segment-based molar fraction mixing rules. This methodology seems to work well for calorimetric properties and volumetric properties.

On the other hand, different empirical mixing rules are needed for transport properties. This is because polymers are viscoelastic, while conventional components exhibit Newtonian behavior, which poses a challenge in developing mixing rules for viscosity of polymer-solvent mixtures.

# PROPERTY MODELS AVAILABLE IN POLYMERS PLUS

Polymers Plus contains several key property models specifically developed for polymer systems. These models consist of two classes:

- Solution thermodynamic models for polymer phase equilibrium calculations (activity coefficient models and equations of state)
- Models for other thermophysical properties (molar volume, enthalpy and heat capacity, entropy, Gibbs energy, transport properties)

These models have been incorporated into several physical property methods. A summary of the available models is provided in Table 3.1. The models are described individually in more detail in the Sections 3-1 to 3-11.

### *Table 3.1 Polymers Plus Thermodynamic and Transport Property Models*

| Model | Description |
|---|---|
| **Enthalpy, heat capacity, and density models** | |
| Van Krevelen models | These models are used for calculating thermodynamic properties of polymer systems using group contribution. A property estimation capacity is available for use with these models |
| Tait model | This model is used to calculate molar volume |
| **Transport property models** | |
| Modified Mark-Houwink models | This model is used to calculate viscosity |
| **Activity coefficient models** | |
| Polymer NRTL model | This model extends the non-random two liquid theory to polymer systems. It accounts for interactions with polymer segments and is well suited for copolymers |
| Flory-Huggins model | This model is the well-known model developed by Flory for representing non-ideality of polymer systems |
| Polymer UNIFAC and Polymer UNIFAC-FV models | These predictive models extend the UNIFAC group contribution method to polymer systems taking into account polymer segments |
| **Equations of State** | |
| Polymer ideal gas model | This model is used together with equations of state to calculate thermodynamic properties |
| Sanchez-Lacombe model | This is a well-known equation of state model, based on the lattice theory, tailored for polymer mixtures |
| Polymer PSRK | This model is an extension of PSRK equation of state to cover polymer mixtures |
| SAFT | This is a rigorous thermodynamic model based on the perturbation theory of fluids |

## Activity Coefficient Models

Models for phase equilibrium calculations of polymer mixtures can be categorized into two groups: *activity coefficient models* and *equations of state*. In general, the activity coefficient models are versatile accommodating a high degree of solution nonideality into the model. On the other hand, when applied to VLE calculations, they can only be used for the liquid phase and another model (usually an equation of state) is needed for the vapor phase. They are used for the calculation of fugacity coefficient enthalpy, entropy and Gibbs energy but are rather cumbersome for evaluation of calorimetric and volumetric properties. Usually other empirical correlations are used in parallel for the calculations of enthalpies and densities when an activity coefficient model is used in phase equilibrium modeling.

There is a large number of activity coefficient models for use in polymer process modeling. Polymers Plus offers the Flory-Huggins model (Flory, 1953), two versions of Non-Random Two-Liquid Activity Coefficient model adopted to polymers (Polymer-NRTL; Chen, 1993), the Polymer UNIFAC model, and the UNIFAC free volume model (Oishi and Prausnitz, 1978). The two UNIFAC models are predictive while the Flory-Huggins and Polymer-NRTL models are correlative. Between the correlative models, the Flory-Huggins model is only applicable to homopolymers because its parameter is polymer-specific. The Polymer-NRTL model is a segment-based model that allows accurate representation of the effects of copolymer composition and polymer chain length.

*Flory-Huggins Model*

The *Flory-Huggins model* is certainly the most well-known solution thermodynamic model used in the industry to correlate the phase behavior of polymer solutions. The model provides a simple and powerful description of the nonideal nature of polymer solutions. The reason for the success of the Flory-Huggins model is its ability to represent the large entropy of mixing due to the chain connectivity of long chain molecules. However, its enthalpy term is merely a first order interaction of nearest neighbors. As a result, the only model parameter $\chi$ often is a strong function of temperature, polymer content of the mixture, and polymer chain length. Therefore, in practice its use for quantitative description of phase behavior of a polymer solution is limited (Koningsveld and Kleintjens, 1971; Qian et al., 1991).

*Polymer-NRTL Model*

The *Polymer-NRTL model* provides a much more practical thermodynamic framework to describe polymer phase behavior by replacing the Flory-Huggins enthalpic term with that of non-random two-liquid theory, while retaining its entropic term (Chen, 1993). The resulting model yields two segment-based binary interaction parameters that are much less dependent to temperature and composition than the Flory $\chi$ parameter. The Polymer-NRTL model is suitable for homopolymers, alternating copolymers, block copolymers, and polymer blends. The most current formulation of this model also takes into account the random copolymers.

The Polymer-NRTL model reduces to the classical NRTL model for conventional components. As such, the NRTL model parameters established for solvents and monomers in the literature can be used directly with the Polymer-NRTL model. Although the Polymer-NRTL model did not consider free volume effect, it has been successfully used to describe vapor-liquid equilibrium and liquid-liquid equilibrium of polymer solutions, including the UCST. Recently, it also has been applied successfully to describe the critical micelle concentration of aqueous nonionic surfactants (Chen, 1996).

*UNIFAC Models*

The UNIFAC models are predictive, and they must be used only in the absence of experimental data. *Polymer UNIFAC* is an extension of the UNIFAC group contribution method developed for standard components to polymer systems. The *UNIFAC free volume* activity coefficient model is the same as the polymer UNIFAC model, except that it contains a term to account for compressibility effects. Thus it has similar capabilities to polymer UNIFAC but is more reliable for VLE predictions at higher pressure than the polymer UNIFAC.

## Equations-of-State

In modeling polymer systems at high pressures, the activity coefficient models suffer from certain shortcomings. For example, most of them are applicable only to incompressible liquid solutions and they fail to predict the LCST type phase behavior that necessitates pressure dependence in a model (Sanchez, 1992). To overcome these difficulties an *equation of state (EOS)* is needed. Another advantage of using an equation of state is the simultaneous calculation of enthalpies and phase densities along with phase equilibrium from the same model.

There is a large number of polymer-specific equations-of-state described in the literature. Currently, the most widely used EOS for polyolefin systems are the *Sanchez-Lacombe* EOS (Sanchez and Lacombe, 1976) and Statistical Associating Fluid Theory EOS (*SAFT*) (Chapman et al., 1989; Xiong and Kiran, 1995; Folie and Radosz, 1995). In addition, well-known cubic equations-of-state for systems with small molecules are being extended for polymer solutions (Kontogeorgis et al., 1994; Saraiva et al., 1996). Presently Polymers Plus offers Sanchez-Lacombe EOS, an extension of the Soave-Redlich-Kwong (SRK) cubic equation of state to polymer-solvent mixtures (*Polymer SRK EOS*) and the SAFT EOS.

The Sanchez-Lacombe and SAFT equations of state are polymer specific, whereas the polymer SRK model is an extension of a conventional cubic EOS to polymers. Polymer specific equations of state have the advantage of describing polymer components of the mixture more accurately. On the other hand, POLYSRK is usually more accurate with the conventional components of a polymer-solvent mixture. The details of the individual EOS models are given in the Section 3.9, Section 3.10 and Section 3.11.

## Other Thermophysical Models

Polymers Plus offers models for the calculations of enthalpy, Gibbs energy, entropy, molar volume (density), and viscosity of pure polymers, and a polymer ideal gas property model.

Van Krevelen (1990) physical property models are used to evaluate enthalpy , Gibbs energy, molar volume in both liquid and solid states, glass transition and melting point temperatures. For molar volume, another alternative is the method of Tait (Danner and High, 1992).

Polymers Plus offers methods for estimation of *zero-shear viscosity of polymer* melts, and also for concentrated polymer solutions. Melt viscosity is calculated using the modified Mark-Houwink/Van Krevelen method (Van Krevelen, 1990). Concentrated polymer solution viscosity is calculated using the Van Krevelen (1990) model.

When an equation of state is used for calculation of enthalpy, entropy and Gibbs energy, it provides only departure values from ideal gas behavior (departure functions). Therefore, in estimating these properties from an equation of state, the ideal gas contribution must be added to the departure functions obtained from the equation of state model. For this purpose, the ideal gas model already available in Aspen Plus for monomers and solvents was extended to polymers and oligomers and made available in Polymers Plus.

# PROPERTY METHODS

One can select a property method from among the already existing property methods in the Polymers Plus package, or create a custom-made property method by modifying an existing property method. The property methods already available in Polymers Plus are listed in Table 3.2.

***Table 3.2 Polymers Plus Property Methods***

| Property method | Description |
|---|---|
| POLYFH | Uses the Flory-Huggins model for solution thermodynamic property calculations and van Krevelen models for thermophysical property calculations |
| POLYNRTL | Uses a polymer NRTL model for solution thermodynamic property calculations and van Krevelen models for thermophysical property calculations |
| POLYUF | Uses a polymer UNIFAC model for solution thermodynamic property calculations and van Krevelen models for thermophysical property calculations |
| POLYUFV | Uses the polymer UNIFAC model with a free volume correction for solution thermodynamic property calculations and van Krevelen models for thermophysical property calculations |
| POLYSL | Uses the Sanchez-Lacombe equation of state model for thermodynamic property calculations |
| POLYSRK | Uses an extension of the Soave-Redlich-Kwong equation of state to polymer systems, with the MHV1 mixing rules and the polymer NRTL excess Gibbs energy model, for thermodynamic property calculations |
| POLYSAFT | Uses the statistical associating fluid theory (SAFT) equation of state for thermodynamic property calculations |

Table 3.3 describes the overall structure of the property methods in terms of the properties calculated for the vapor and liquid phases and the models used for the property calculations are given.

### *Table 3.3 Polymers Plus Property Method Structure*

| Properties Calculated | Model (Property method) | Used For | Required Parameters |
|---|---|---|---|
| **Vapor** | | | |
| Departure functions, fugacity coefficient, molar volume | Redlich-Kwong<br>(All activity coefficient property methods) | All vapor properties, i.e. Fugacity coefficient, enthalpy, entropy, free energy | TC, PC |
| | Sanchez-Lacombe (POLYSL) | All vapor properties, i.e. Fugacity coefficient, enthalpy, entropy, free energy | SLTSTR, SLPSTR, SLRSTR, CPIG |
| | Polymer SRK (POLYSRK) | All vapor properties, i.e. Fugacity coefficient, enthalpy, entropy, free energy | TCRKS, PCRKS, RKSMCP, CPIG |
| | SAFT EOS (POLYSAFT) | All liquid properties, i.e., Fugacity coefficient, enthalpy, entropy, free energy | SAFTM, SAFTV, SAFTU, SFTEPS, CPIG |
| **Liquid** | | | |
| Vapor pressure PLXANT | Antoine<br>(All activity coefficient property methods) | | |
| Activity Coefficient | Flory-Huggins (POLYFH) | Fugacity coefficient, free energy, enthalpy, entropy | FHCHI, FHSIZE |
| | Polymer NRTL (POLYNRTL) | Fugacity coefficient, free energy, enthalpy, entropy | NRTL |
| | Polymer UNIFAC (POLYUF) | Fugacity coefficient, free energy, enthalpy, entropy | N/A |
| | UNIFAC free volume (POLYUFV) | Fugacity coefficient, free energy, enthalpy, entropy | N/A |
| Vaporization enthalpy | Watson for monomers Van Krevelen for polymers and oligomers from segments<br>(All activity coefficient property methods) | Enthalpy, entropy | TC, DHVLWT or DHVLDP |
| Molar Volume | Rackett for monomers Van Krevelen for polymers and oligomers from segments<br>(All activity coefficient property methods) | Density | TC, PC, VCRKT or VC, RKTZRA or ZC, DNLDIP |
| Departure functions, fugacity coefficient, molar volume | Sanchez-Lacombe (POLYSL) | All liquid properties, i.e. Fugacity coefficient, enthalpy, entropy, free energy, density | SLTSTR, SLPSTR, SLRSTR, CPIG |
| | Polymer SRK (POLYSRK) | All liquid properties, i.e. Fugacity coefficient, enthalpy, entropy, free energy, density | TCRKS, PCRKS, RKSMCP, CPIG |
| | SAFT EOS (POLYSAFT) | All liquid properties, i.e. Fugacity coefficient, enthalpy, entropy, free energy, density | SAFTM, SAFTV, SAFTU, SFTEPS, CPIG |

# THERMODYNAMIC DATA FOR POLYMERS

The data published in the literature for pure polymers and for polymer solutions is very limited in comparison to the enormous amount of vapor-liquid equilibrium data available for mixtures of small molecules (Wohlfarth, 1994). The AIChE-DIPPR handbook of polymer solution thermodynamics (Danner and High, 1992) provides a computer database for pure polymer pressure-volume-temperature data, finite concentration VLE data, infinite dilution VLE data, binary liquid-liquid equilibria data, and ternary liquid-liquid equilibria data. The DECHEMA polymer solution data collection contains data for VLE, solvent activity coefficients at infinite dilution, and liquid-liquid equilibrium (Hao et al., 1992).

Another data source for polymer properties is the compilation of Wohlfarth (1994). Wohlfarth compiled VLE data for polymer systems in three groups: vapor pressures of binary polymer solutions (or solvent activities), segment-based excess Gibbs free energies of binary polymer solutions, and weight fraction Henry-constants for gases and vapors in molten polymers.

In another useful source, Barton (1990) presented a comprehensive compilation of cohesion parameters for polymers as well as polymer-liquid Flory-Huggins interaction parameter $\chi$.

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# 3.1 VAN KREVELEN PROPERTY MODELS

This section describes the correlations used in each of the van Krevelen thermophysical property models. A description of the group contribution method is also given.

Topics covered include:

- Summary of Applicability
- Liquid Enthalpy Model
- Solid Enthalpy Model
- Liquid Gibbs Free Energy
- Solid Gibbs Free Energy Model
- Liquid Molar Volume Model
- Solid Molar Volume Model
- Glass Transition Temperature Correlation
- Melt Transition Temperature Correlation
- Van Krevelen Property Parameter Estimation
- Specifying Physical Properties

## SUMMARY OF APPLICABILITY

The van Krevelen thermophysical property models are used to calculate density, enthalpy, entropy, Gibbs free energy, and heat capacity for polymers, oligomers, and segments. The van Krevelen models are incorporated in various Polymers Plus property methods, and are used in heat and mass balance calculations. These models can be used in predictive mode (as group-contribution methods), or in a correlative mode (in the case there is experimental information available for parameter estimation).

# VAN KREVELEN MODELS

The van Krevelen models are used to calculate polymer enthalpy, Gibbs free energy and molar volume (i.e. density) in several physical property methods. These properties are essential for heat and mass balance calculations.

The van Krevelen thermophysical models have been implemented in Polymers Plus as polynomial expressions. Table 3.4 lists models available. Note that these models only apply to polymers, oligomers, and segments. Solvents and monomers make use of models already available in Aspen Plus. In order to provide the necessary model input parameters, users may make use of the Aspen Plus Data Regression capability. However, a property estimation method using the van Krevelen group contribution method is available in Polymers Plus.

For polymers and oligomers, in most cases, the models provide separate correlations for the crystalline phase and the liquid phase. Depending on the temperature region being considered, above the melt transition temperature, between the melt and glass transition temperature, or below the glass transition temperature, one or both correlations may apply. When the temperature region is between the melt transition temperature and the glass transition temperature, the contribution of each correlation is determined by the degree of crystallinity which is one of the model input parameters. Correlations for estimating the melt and glass transition temperature are also provided.

***Table 3.4 Van Krevelen Property Models***

| Property Name | Description |
|---|---|
| HL | Liquid enthalpy |
| HS | Solid enthalpy |
| GL | Liquid Gibbs free energy |
| GS | Solid Gibbs free energy |
| VL | Liquid molar volume (density) |
| VS | Solid molar volume (density) |
| TG | Glass transition temperature |
| TM | Melt transition temperature |

# LIQUID ENTHALPY MODEL

The liquid enthalpy model correlations are given below:

$$HL = H_l \quad \text{for} \quad T > T_m$$

$$= H_c x_c + H_l(1 - x_c) \quad \text{for} \quad T < T_m$$

With:

*Liquid Enthalpy*

$$H_l = H^o_{l,ref}(298K) + \int_{298}^{T} Cp_l dT \tag{3.1}$$

$$H^o_{l,ref}(298K) = \Delta H^o_f(IG,298K) + \Delta H^o_{cond}(298K) \tag{3.2}$$

$$H_c = H^o_{c,ref}(298K) + \int_{298}^{T} Cp_c dT \tag{3.3}$$

$$H^o_{c,ref}(298K) = \Delta H^o_f(IG,298K) - \Delta H^o_{sub}(298K) \tag{3.4}$$

Where:

$x_c$ = crystallinity

*Cp* = heat capacity for the polymer

Subscript *c* refers to the crystalline state, and subscript *l* refers to the liquid state.

*Cp* for polymers and oligomers is calculated using the polynomial expressions:

*Heat Capacity*

$$Cp_l = A + BT + CT^2 + DT^3 \quad \text{for} \quad E < T < F \tag{3.5}$$

$$Cp_c = A' + B'T + C'T^2 + D'T^3 \quad \text{for} \quad E' < T < F' \tag{3.6}$$

where *A*-*F* and *A'*-*F'* are user specified coefficients and temperature bounds.

Users may enter the *Cp* coefficients for the polymer or oligomer, or for the segments. If coefficients are entered for the segments, the polymer or the oligomer *Cp* is calculated from the segment *Cp* values. If no coefficients are provided for either the polymer, oligomer or segments, *Cp* values for segments are estimated using group contribution:

| | | |
|---|---|---|
| $\Delta H_f$ | = | enthalpy of formation |
| $H_{ref}$ | = | reference enthalpy |
| $\Delta H_{cond}$ | = | enthalpy of condensation |
| $\Delta H_{sub}$ | = | enthalpy of sublimation |
| $T_m$ | = | melt transition temperature |
| $T_g$ | = | glass transition temperature |

Figure 3.3 shows the various regions of applicability for the correlations.

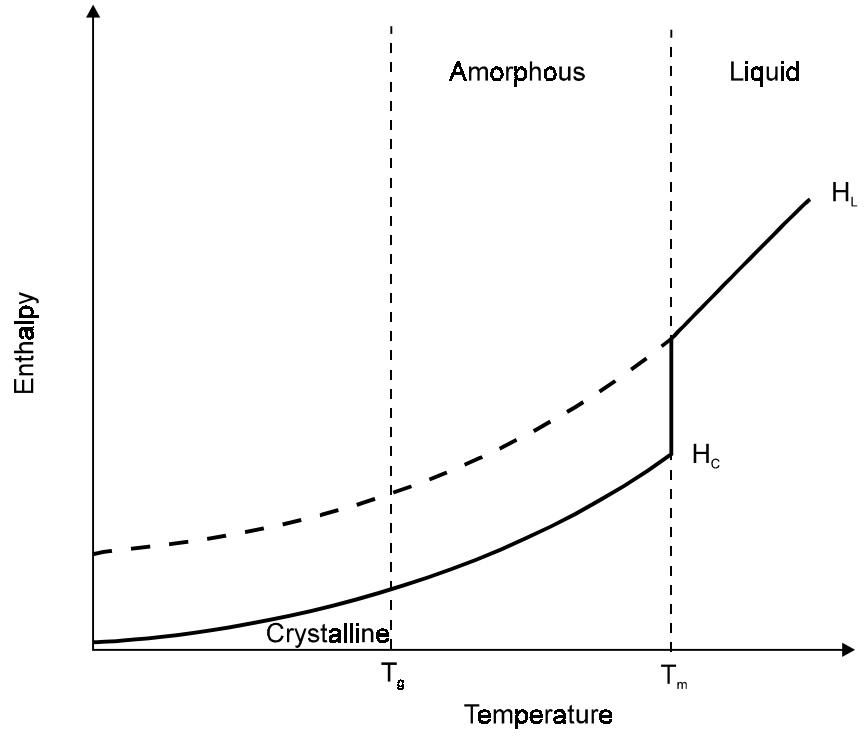



***Figure 3.3*** *Polymer Enthalpy as a Function of Temperature*

## Liquid Enthalpy Model Parameters

The enthalpy model parameters are given in Table 3.5. An estimation method is available to determine these parameters. See Van Krevelen Property Parameter Estimation later in this section. The parameters are mole based. Users have the option of entering mass based parameters for polymers and oligomers but not for segments. See Appendix E for a list of corresponding mass based parameters.

### Table 3.5 Liquid Enthalpy Model Parameters

| Parameter Name / Element | Symbol | Default | Units Keyword | SI Units | Comments |
|---|---|---|---|---|---|
| CPLVK/1 | $A$ | -- | MOLE-HEAT-CAPACITY | $J / KMOL - K$ | Unary |
| CPLVK/2 | $B$ | -- | MOLE-HEAT-CAPACITY, TEMPERATURE | $J / KMOL - K^2$ | Unary |
| CPLVK/3 | $C$ | -- | MOLE-HEAT-CAPACITY, TEMPERATURE | $J / KMOL - K^3$ | Unary |
| CPLVK/4 | $D$ | -- | MOLE-HEAT-CAPACITY, TEMPERATURE | $J / KMOL - K^4$ | Unary |
| CPLVK/5 | $E$ | 0D0 | TEMPERATURE | $K$ | Unary |
| CPLVK/6 | $F$ | 1D3 | TEMPERATURE | $K$ | Unary |
| CPCVK/1 | $A'$ | -- | MOLE-HEAT-CAPACITY | $J / KMOL - K$ | Unary |
| CPCVK/2 | $B'$ | -- | MOLE-HEAT-CAPACITY, TEMPERATURE | $J / KMOL - K^2$ | Unary |
| CPCVK/3 | $C'$ | -- | MOLE-HEAT-CAPACITY, TEMPERATURE | $J / KMOL - K^3$ | Unary |
| CPCVK/4 | $D'$ | -- | MOLE-HEAT-CAPACITY, TEMPERATURE | $J / KMOL - K^4$ | Unary |
| CPCVK/5 | $E'$ | 0D0 | TEMPERATURE | $K$ | Unary |
| CPCVK/6 | $F'$ | 1D3 | TEMPERATURE | $K$ | Unary |
| DHFVK | $\Delta H_f^o$ | -- | MOLE- ENTHALPY | $J / KMOL$ | Unary |
| DHCON | $\Delta H_{con}^o$ | -7D6 | MOLE-ENTHALPY | $J / KMOL$ | Unary |
| DHSUB | $\Delta H_{sub}^o$ | 1.7D7 | MOLE-ENTHALPY | $J / KMOL$ | Unary |
| POLCRY | $x_c$ | 0.0 | -- | -- | Unary |
| TGVK | $Tg$ | -- | TEMPERATURE | $K$ | Unary |
| TMVK | $Tm$ | -- | TEMPERATURE | $K$ | Unary |

# SOLID ENTHALPY MODEL

The solid enthalpy model correlations are given below:

$$HS = H_c x_c + H_l(1 - x_c) \quad \text{for} \quad T_g < T < T_m$$

$$= H_c \quad \text{for} \quad T < T_g$$

With:

$$H_l = H^o_{l,ref}(298K) + \int_{298}^{T} Cp_l dT \tag{3.1}$$

$$H^o_{l,ref}(298K) = \Delta H^o_f(IG,298K) + \Delta H^o_{cond}(298K) \tag{3.2}$$

$$H_c = H^o_{c,ref}(298K) + \int_{298}^{T} Cp_c dT \tag{3.3}$$

$$H^o_{c,ref}(298K) = \Delta H^o_f(IG,298K) - \Delta H^o_{sub}(298K) \tag{3.4}$$

Where:

$x_c$ = crystallinity

$Cp$ = heat capacity for the polymer

Subscript *c* refers to the crystalline state, and subscript *l* refers to the liquid state.

$Cp$ for polymers and oligomers is calculated using the polynomial expressions:

$$Cp_l = A + BT + CT^2 + DT^3 \quad \text{for} \quad E < T < F \tag{3.5}$$

$$Cp_c = A' + B'T + C'T^2 + D'T^3 \quad \text{for} \quad E' < T < F' \tag{3.6}$$

where *A*-*F* and *A′*-*F′* are user specified coefficients and temperature bounds.

Users may enter the *Cp* coefficients for the polymer or oligomer, or for the segments. If coefficients are entered for the segments, the polymer or the oligomer *Cp* is calculated from the segment *Cp* values. If no coefficients are provided for either the polymer, oligomer or segments, *Cp* values for segments are estimated using group contribution:

$\Delta H_f$ = enthalpy of formation

$H_{ref}$ = reference enthalpy

$\Delta H_{cond}$ = enthalpy of condensation

$\Delta H_{sub}$ = enthalpy of sublimation

$T_m$ = melt transition temperature

$T_g$ = glass transition temperature

## Solid Enthalpy Model Parameters

The enthalpy model parameters are given in Table 3.6. An estimation method is available to determine these parameters (See Van Krevelen Property Parameter Estimation). The parameters are mole based. Users have the option of entering mass based parameters for polymers and oligomers but not for segments. See Appendix E for a list of corresponding mass based parameters.

The various regions of applicability for the correlations were shown in Figure 3.3.

### *Table 3.6 Solid Enthalpy Model Parameters*

| Parameter Name / Element | Symbol | Default | Units Keyword | SI Units | Comments |
|---|---|---|---|---|---|
| CPLVK/1 | $A$ | -- | MOLE-HEAT-CAPACITY | $J / KMOL - K$ | Unary |
| CPLVK/2 | $B$ | -- | MOLE-HEAT-CAPACITY, TEMPERATURE | $J / KMOL - K^2$ | Unary |
| CPLVK/3 | $C$ | -- | MOLE-HEAT-CAPACITY, TEMPERATURE | $J / KMOL - K^3$ | Unary |
| CPLVK/4 | $D$ | -- | MOLE-HEAT-CAPACITY, TEMPERATURE | $J / KMOL - K^4$ | Unary |
| CPLVK/5 | $E$ | 0D0 | TEMPERATURE | $K$ | Unary |
| CPLVK/6 | $F$ | 1D3 | TEMPERATURE | $K$ | Unary |
| CPCVK/1 | $A'$ | -- | MOLE-HEAT-CAPACITY | $J / KMOL - K$ | Unary |
| CPCVK/2 | $B'$ | -- | MOLE-HEAT-CAPACITY, TEMPERATURE | $J / KMOL - K^2$ | Unary |
| CPCVK/3 | $C'$ | -- | MOLE-HEAT-CAPACITY, TEMPERATURE | $J / KMOL - K^3$ | Unary |
| CPCVK/4 | $D'$ | -- | MOLE-HEAT-CAPACITY, TEMPERATURE | $J / KMOL - K^4$ | Unary |
| CPCVK/5 | $E'$ | 0D0 | TEMPERATURE | $K$ | Unary |
| CPCVK/6 | $F'$ | 1D3 | TEMPERATURE | $K$ | Unary |
| DHFVK | $\Delta H_f^o$ | -- | MOLE- ENTHALPY | $J / KMOL$ | Unary |
| DHCON | $\Delta H_{con}^o$ | -7D6 | MOLE-ENTHALPY | $J / KMOL$ | Unary |
| DHSUB | $\Delta H_{sub}^o$ | 1.7D7 | MOLE-ENTHALPY | $J / KMOL$ | Unary |
| POLCRY | $x_c$ | 0.0 | -- | -- | Unary |
| TGVK | $Tg$ | -- | TEMPERATURE | $K$ | Unary |
| TMVK | $Tm$ | -- | TEMPERATURE | $K$ | Unary |

# LIQUID GIBBS FREE ENERGY MODEL

The liquid Gibbs free energy model correlations are given below:

$$GL = G_l \quad \text{for} \quad T > T_m$$

$$= G_c x_c + G_l(1 - x_c) \quad \text{for} \quad T_g < T < T_m$$

$$= G_c \quad \text{for} \quad T < T_g$$

With:

*Liquid Gibbs Energy*

$$G_l = G^o_{l,ref}(298K) + \int_{298}^{T} Cp_l dT - T\int_{298}^{T} \frac{Cp_l}{T} dT - (T - 298K)\Delta S^o_f(IG,298K) - (T - 298K)\Delta S^o_{cond}(298K) \quad \textbf{(3.7)}$$

$$G^o_{l,ref}(298K) = \Delta G^o_f(IG,298K) + \Delta G^o_{cond}(298K) \quad \textbf{(3.8)}$$

$$\Delta S^o_f(IG,298K) = \frac{\left[\Delta H^o_f(IG,298K) - \Delta G^o_f(IG,298K)\right]}{298K} \quad \textbf{(3.9)}$$

$$\Delta S^o_{cond}(298K) = \frac{\left[\Delta H^o_{cond} - \Delta G^o_{cond}\right]}{298K} \quad \textbf{(3.10)}$$

$$G_c = G^o_{c,ref}(298K) + \int_{298}^{T} Cp_c dT - T\int_{298}^{T} \frac{Cp_c}{T} dT \quad \textbf{(3.11)}$$

$$G^o_{c,ref}(298K) = \Delta G^o_f(IG,298K) - \Delta G^o_{sub}(298K) \quad \textbf{(3.12)}$$

Where:

$x_c$ = crystallinity

$Cp$ = heat capacity for the polymer

Subscript *c* refers to the crystalline state, and subscript *l* refers to the liquid state.

$Cp$ for polymers and oligomers is calculated using the polynomial expressions:

$$Cp_l = A + BT + CT^2 + DT^3 \quad \text{for} \quad E < T < F \quad \textbf{(3.5)}$$

$$Cp_c = A' + B'T + C'T^2 + D'T^3 \quad \text{for} \quad E' < T < F' \quad \textbf{(3.6)}$$

where *A*-*F* and *A'*-*F'* are user specified coefficients.

Users may enter the *Cp* coefficients for the polymer or oligomer, or for the segments. If coefficients are entered for the segments, the polymer or the oligomer *Cp* is calculated from the segment *Cp* values. If no coefficients are provided for either the polymer, oligomer or segments, *Cp* values for segments are estimated using group contribution:

$\Delta G_f$ = Gibbs free energy of formation

$\Delta G_{cond}$ = Gibbs free energy of condensation

$\Delta G_{sub}$ = Gibbs free energy of sublimation

$G_{ref}$ = reference Gibbs free energy

$T_m$ = melt transition temperature

$T_g$ = glass transition temperature

## Liquid Gibbs Free Energy Model Parameters

The Gibbs free energy model parameters are given in Table 3.7. An estimation method is available to determine these parameters (See Van Krevelen Property Parameter Estimation). The parameters are mole based. Users have the option of entering mass based parameters for polymers and oligomers but not for segments. See Appendix E for a list of corresponding mass based parameters.

### Table 3.7 Liquid Gibbs Free Energy Model Parameters

| Parameter Name / Element | Symbol | Default | Units Keyword | SI Units | Comments |
|---|---|---|---|---|---|
| CPLVK/1 | $A$ | -- | MOLE-HEAT-CAPACITY | $J / KMOL - K$ | Unary |
| CPLVK/2 | $B$ | -- | MOLE-HEAT-CAPACITY, TEMPERATURE | $J / KMOL - K^2$ | Unary |
| CPLVK/3 | $C$ | -- | MOLE-HEAT-CAPACITY, TEMPERATURE | $J / KMOL - K^3$ | Unary |
| CPLVK/4 | $D$ | -- | MOLE-HEAT-CAPACITY, TEMPERATURE | $J / KMOL - K^4$ | Unary |
| CPLVK/5 | $E$ | 0D0 | TEMPERATURE | $K$ | Unary |
| CPLVK/6 | $F$ | 1D3 | TEMPERATURE | $K$ | Unary |
| CPCVK/1 | $A'$ | -- | MOLE-HEAT-CAPACITY | $J / KMOL - K$ | Unary |
| CPCVK/2 | $B'$ | -- | MOLE-HEAT-CAPACITY, TEMPERATURE | $J / KMOL - K^2$ | Unary |
| CPCVK/3 | $C'$ | -- | MOLE-HEAT-CAPACITY, TEMPERATURE | $J / KMOL - K^3$ | Unary |
| CPCVK/4 | $D'$ | -- | MOLE-HEAT-CAPACITY, TEMPERATURE | $J / KMOL - K^4$ | Unary |
| CPCVK/5 | $E'$ | 0D0 | TEMPERATURE | $K$ | Unary |
| CPCVK/6 | $F'$ | 1D3 | TEMPERATURE | $K$ | Unary |
| DGFVK | $\Delta G_f^o$ | -- | MOLE- ENTHALPY | $J / KMOL$ | Unary |
| DGCON | $\Delta G_{con}^o$ | -2.528D6 | MOLE-ENTHALPY | $J / KMOL$ | Unary |
| DGSUB | $\Delta G_{sub}^o$ | 5.074D6 | MOLE-ENTHALPY | $J / KMOL$ | Unary |
| POLCRY | $x_c$ | 0.0 | -- | -- | Unary |
| TGVK | $Tg$ | -- | TEMPERATURE | $K$ | Unary |
| TMVK | $Tm$ | -- | TEMPERATURE | $K$ | Unary |

# SOLID GIBBS FREE ENERGY MODEL

The solid Gibbs energy model correlations are given below:

$$GS = G_c x_c + G_l(1 - x_c) \quad \text{for} \quad T_g < T < T_m$$

$$= G_c \quad \text{for} \quad T < T_g$$

With:

$$G_l = G^o_{l,ref}(298K) + \int_{298}^{T} Cp_l dT - T\int_{298}^{T} \frac{Cp_l}{T} dT - (T - 298K)\Delta S^o_f(IG,298K) - (T - 298K)\Delta S^o_{cond}(298K) \quad \textbf{(3.7)}$$

$$G^o_{l,ref}(298K) = \Delta G^o_f(IG,298K) + \Delta G^o_{cond}(298K) \quad \textbf{(3.8)}$$

$$\Delta S^o_f(IG,298K) = \frac{\left[\Delta H^o_f(IG,298K) - \Delta G^o_f(IG,298K)\right]}{298K} \quad \textbf{(3.9)}$$

$$\Delta S^o_{cond}(298K) = \frac{\left[\Delta H^o_{cond} - \Delta G^o_{cond}\right]}{298K} \quad \textbf{(3.10)}$$

$$G_c = G^o_{c,ref}(298K) + \int_{298}^{T} Cp_c dT - T\int_{298}^{T} \frac{Cp_c}{T} dT - (T - 298K)\Delta S^o_f(IG,298K) - (T - 298K)\Delta S^o_{sub}(IG,298K) \quad \textbf{(3.13)}$$

$$G^o_{c,ref}(298K) = \Delta G^o_f(IG,298K) - \Delta G^o_{sub}(298K) \quad \textbf{(3.12)}$$

$$\Delta S^o_{sub}(298K) = \frac{\left[\Delta H^o_{sub} - \Delta G^o_{sub}\right]}{298K} \quad \textbf{(3.14)}$$

Where:

$x_c$ = crystallinity

$Cp$ = heat capacity for the polymer

Subscript *c* refers to the crystalline state, and subscript *l* refers to the liquid state.

$Cp$ for polymers and oligomers is calculated using the polynomial expressions:

$$Cp_l = A + BT + CT^2 + DT^3 \quad \text{for} \quad E < T < F \quad \textbf{(3.5)}$$

$$Cp_c = A' + B'T + C'T^2 + D'T^3 \quad \text{for} \quad E' < T < F' \quad \textbf{(3.6)}$$

where *A*-*F* and *A'*-*F'* are user specified coefficients.

Users may enter the *Cp* coefficients for the polymer or oligomer, or for the segments. If coefficients are entered for the segments, the polymer or the oligomer *Cp* is calculated from the segment *Cp* values. If no coefficients are provided for either the polymer, oligomer or segments, *Cp* values for segments are estimated using group contribution:

$\Delta G_f$ = Gibbs free energy of formation

$\Delta G_{cond}$ = Gibbs free energy of condensation

$\Delta G_{sub}$ = Gibbs free energy of sublimation

$G_{ref}$ = reference Gibbs free energy

$T_m$ = melt transition temperature

$T_g$ = glass transition temperature

## Solid Gibbs Free Energy Model Parameters

The Gibbs free energy model parameters are given in Table 3.8. An estimation method is available to determine these parameters (See Van Krevelen Property Parameter Estimation). The parameters are mole based. Users have the option of entering mass based parameters for polymers and oligomers but not for segments. See Appendix E for a list of corresponding mass based parameters.

### Table 3.8 Solid Gibbs Free Energy Model Parameters

| Parameter Name / Element | Symbol | Default | Units Keyword | SI Units | Comments |
|---|---|---|---|---|---|
| CPLVK/1 | $A$ | -- | MOLE-HEAT-CAPACITY | $J / KMOL - K$ | Unary |
| CPLVK/2 | $B$ | -- | MOLE-HEAT-CAPACITY, TEMPERATURE | $J / KMOL - K^2$ | Unary |
| CPLVK/3 | $C$ | -- | MOLE-HEAT-CAPACITY, TEMPERATURE | $J / KMOL - K^3$ | Unary |
| CPLVK/4 | $D$ | -- | MOLE-HEAT-CAPACITY, TEMPERATURE | $J / KMOL - K^4$ | Unary |
| CPLVK/5 | $E$ | 0D0 | TEMPERATURE | $K$ | Unary |
| CPLVK/6 | $F$ | 1D3 | TEMPERATURE | $K$ | Unary |
| CPCVK/1 | $A'$ | -- | MOLE-HEAT-CAPACITY | $J / KMOL - K$ | Unary |
| CPCVK/2 | $B'$ | -- | MOLE-HEAT-CAPACITY, TEMPERATURE | $J / KMOL - K^2$ | Unary |
| CPCVK/3 | $C'$ | -- | MOLE-HEAT-CAPACITY, TEMPERATURE | $J / KMOL - K^3$ | Unary |
| CPCVK/4 | $D'$ | -- | MOLE-HEAT-CAPACITY, TEMPERATURE | $J / KMOL - K^4$ | Unary |
| CPCVK/5 | $E'$ | 0D0 | TEMPERATURE | $K$ | Unary |
| CPCVK/6 | $F'$ | 1D3 | TEMPERATURE | $K$ | Unary |
| DGFVK | $\Delta G_f^o$ | -- | MOLE- ENTHALPY | $J / KMOL$ | Unary |
| DGCON | $\Delta G_{con}^o$ | -2.528D6 | MOLE-ENTHALPY | $J / KMOL$ | Unary |
| DGSUB | $\Delta G_{sub}^o$ | 5.074D6 | MOLE-ENTHALPY | $J / KMOL$ | Unary |
| POLCRY | $x_c$ | 0.0 | -- | -- | Unary |
| TGVK | $Tg$ | -- | TEMPERATURE | $K$ | Unary |
| TMVK | $Tm$ | -- | TEMPERATURE | $K$ | Unary |

# LIQUID MOLAR VOLUME MODEL

The liquid molar volume model correlations are given below:

$$VL = V_l \quad \text{for} \quad T > T_m$$

$$= V_c x_c + V_l(1 - x_c) \quad \text{for} \quad T_g < T < T_m$$

$$= V_c x_c + V_g(1 - x_c) \quad \text{for} \quad T < T_g$$

Where:

$x_c$ = crystallinity

subscript *l* refers to the liquid state

subscript *c* refers to the crystalline state

subscript *g* refers to the glassy state

$V_l$, $V_c$, $V_g$ for polymers and oligomers are calculated from segment properties using:

$$V_l = Mw_n / M_{seg} \sum f_j M_j / \rho_{l,j} \quad \textbf{(3.15)}$$

$$V_c = Mw_n / M_{seg} \sum f_j M_j / \rho_{c,j} \quad \textbf{(3.16)}$$

$$V_g = Mw_n / M_{seg} \sum f_j M_j / \rho_{g,j} \quad \textbf{(3.17)}$$

Where:

$Mw_n$ = polymer number average molecular weight

$M_{seg}$ = average molecular weight of segments

$f_j$ = segment fraction

$M_j$ = molecular weight of segment

$\rho$ = mass density

$\rho$ is calculated from polynomial expressions as:

$$\rho_{l,j} = A/(1 + BT) \quad \text{for} \quad C < T < D \quad \textbf{(3.18)}$$

$$\rho_{c,j} = A'/(1 + B'T) \quad \text{for} \quad C' < T < D' \quad \textbf{(3.19)}$$

$$\rho_{g,j} = A''/(1 + B''T + C''T_g) \quad \text{for} \quad D'' < T < E'' \quad \textbf{(3.20)}$$

Users may enter the ρ coefficients for the polymer or oligomer or for the segment. If coefficients are entered for the segments, the polymer or oligomer ρ is calculated from the segment ρ values. If no coefficients are provided for either the polymer, oligomer or segments, ρ for segments is estimated using the functional group van der Waals volume:

$$\rho_{l,j} = \frac{1}{V_{l,j}(T)}$$

$$V_{l,j}(T) = \sum_k n_k V_k(T) \qquad \text{(for segments)}$$

$$V_k(T) = V_w(a + bT + cT_g) \qquad \text{(for functional groups)}$$

Where:

$n_k$ = number of occurrences of group $k$ in segment $j$

$V_w$ = van der Waals volume of group $k$

$T_g$ = glass transition temperature

Figure 3.4 shows the various regions of applicability for the correlations.

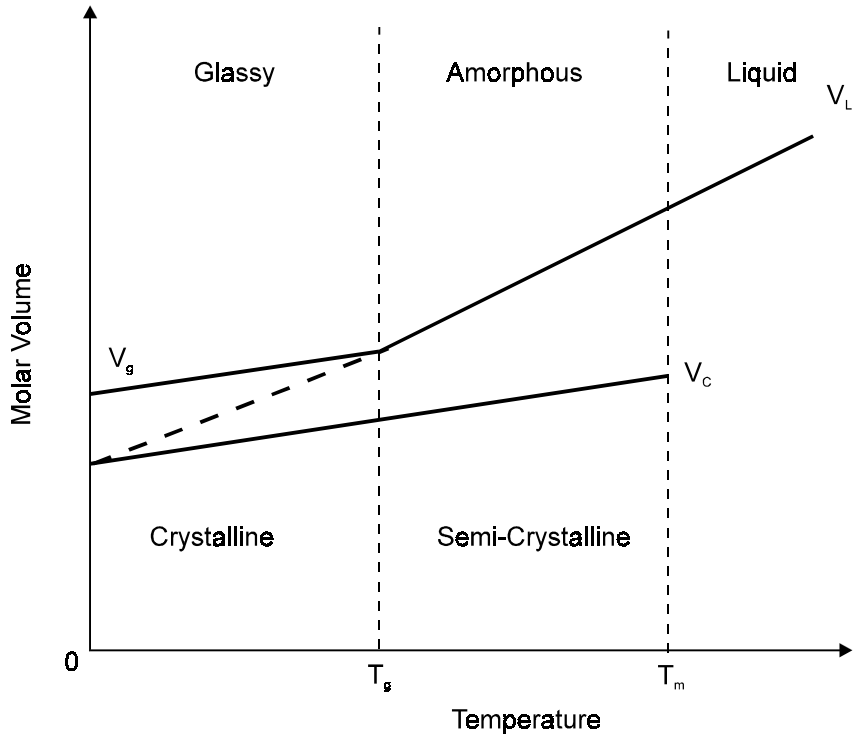



***Figure 3.4*** *Polymer Molar Volume as a Function of Temperature*

## Liquid Molar Volume Model Parameters

The molar volume model parameters are given in Table 3.9. An estimation method is available to determine these parameters (See Van Krevelen Property Parameter Estimation). The parameters are mole based. Users have the option of entering mass based parameters for polymers and oligomers but not for segments. See Appendix E for a list of mass based parameters.

***Table 3.9 Liquid Molar Volume Model Parameters***

| Parameter Name / Element | Symbol | Default | Units Keyword | SI Units | Comments |
|---|---|---|---|---|---|
| DNLVK/1 | $A$ | -- | MOLE-DENSITY | $KMOL / CUM$ | Unary |
| DNLVK/2 | $B$ | -- | TEMPERATURE | $K^{-1}$ | Unary |
| DNLVK/3 | $C$ | 0D0 | TEMPERATURE | $K$ | Unary |
| DNLVK/4 | $D$ | 1D3 | TEMPERATURE | $K$ | Unary |
| DNCVK/1 | $A'$ | -- | MOLE-DENSITY | $KMOL / CUM$ | Unary |
| DNCVK/2 | $B'$ | -- | TEMPERATURE | $K^{-1}$ | Unary |
| DNCVK/3 | $C'$ | 0D0 | TEMPERATURE | $K$ | Unary |
| DNCVK/4 | $D'$ | 1D3 | TEMPERATURE | $K$ | Unary |
| DNGVK/1 | $A''$ | -- | MOLE-DENSITY | $KMOL / CUM$ | Unary |
| DNGVK/2 | $B''$ | -- | TEMPERATURE | $K^{-1}$ | Unary |
| DNGVK/3 | $C''$ | -- | TEMPERATURE | $K^{-1}$ | Unary |
| DNGVK/4 | $D''$ | 0D0 | TEMPERATURE | $K$ | Unary |
| DNGVK/5 | $E''$ | 1D3 | TEMPERATURE | $K$ | Unary |
| POLCRY | $x_c$ | 0.0 | -- | -- | Unary |
| TGVK | $Tg$ | -- | TEMPERATURE | $K$ | Unary |
| TMVK | $Tm$ | -- | TEMPERATURE | $K$ | Unary |

# SOLID MOLAR VOLUME MODEL

The solid molar volume model correlations are given below:

$$VS = V_c x_c + V_l(1 - x_c) \quad \text{for} \quad T_g < T < T_m$$

$$= V_c x_c + V_g(1 - x_c) \quad \text{for} \quad T < T_g$$

Where:

$x_c$ = crystallinity

subscript *l* refers to the liquid state

subscript *c* refers to the crystalline state

subscript *g* refers to the glassy state

$V_l$, $V_c$, $V_g$ for polymers and oligomers are calculated from segment properties using:

$$V_l = Mw_n / M_{seg} \sum f_j M_j / \rho_{l,j} \quad \textbf{(3.15)}$$

$$V_c = Mw_n / M_{seg} \sum f_j M_j / \rho_{c,j} \quad \textbf{(3.16)}$$

$$V_g = Mw_n / M_{seg} \sum f_j M_j / \rho_{g,j} \quad \textbf{(3.17)}$$

Where:

$Mw_n$ = polymer number average molecular weight

$M_{seg}$ = average molecular weight of segments

$f_j$ = segment fraction

$M_j$ = molecular weight of segment

$\rho$ = mass density

$\rho$ is calculated from polynomial expressions as:

$$\rho_{l,j} = A/(1 + BT) \quad \text{for} \quad C < T < D \quad \textbf{(3.18)}$$

$$\rho_{c,j} = A'/(1 + B'T) \quad \text{for} \quad C' < T < D' \quad \textbf{(3.19)}$$

$$\rho_{g,j} = A''/(1 + B''T + C''T_g) \quad \text{for} \quad D'' < T < E'' \quad \textbf{(3.20)}$$

Users may enter the ρ coefficients for the polymer or oligomer or for the segment. If coefficients are entered for the segments, the polymer or oligomer ρ is calculated from the segment ρ values. If no coefficients are provided for either the polymer, oligomer or segments, ρ for segments is estimated using the functional group van der Waals volume:

$$\rho_{l,j} = \frac{1}{V_{l,j}(T)}$$

$$V_{l,j}(T) = \sum_k n_k V_k(T) \qquad \text{(for segments)}$$

$$V_k(T) = V_w(a + bT + cT_g) \qquad \text{(for functional groups)}$$

Where:

$n_k$ = number of occurrences of group *k* in segment *j*

$V_w$ = van der Waals volume of group *k*

$T_g$ = glass transition temperature

## Solid Molar Volume Model Parameters

The molar volume model parameters are given in Table 3.10. An estimation method is available to determine these parameters (See Van Krevelen Property Parameter Estimation). The parameters are mole based. Users have the option of entering mass based parameters for polymers and oligomers but not for segments. See Appendix E for a list of mass based parameters.

The various regions of applicability for the correlations were shown in Figure 3.4.

### Table 3.10 Solid Molar Volume Model Parameters

| Parameter Name / Element | Symbol | Default | Units Keyword | SI Units | Comments |
|---|---|---|---|---|---|
| DNLVK/1 | $A$ | -- | MOLE-DENSITY | $KMOL / CUM$ | Unary |
| DNLVK/2 | $B$ | -- | TEMPERATURE | $K^{-1}$ | Unary |
| DNLVK/3 | $C$ | 0D0 | TEMPERATURE | $K$ | Unary |
| DNLVK/4 | $D$ | 1D3 | TEMPERATURE | $K$ | Unary |
| DNCVK/1 | $A'$ | -- | MOLE-DENSITY | $KMOL / CUM$ | Unary |
| DNCVK/2 | $B'$ | -- | TEMPERATURE | $K^{-1}$ | Unary |
| DNCVK/3 | $C'$ | 0D0 | TEMPERATURE | $K$ | Unary |
| DNCVK/4 | $D'$ | 1D3 | TEMPERATURE | $K$ | Unary |
| DNGVK/1 | $A''$ | -- | MOLE-DENSITY | $KMOL / CUM$ | Unary |
| DNGVK/2 | $B''$ | -- | TEMPERATURE | $K^{-1}$ | Unary |
| DNGVK/3 | $C''$ | -- | TEMPERATURE | $K^{-1}$ | Unary |
| DNGVK/4 | $D''$ | 0D0 | TEMPERATURE | $K$ | Unary |
| DNGVK/5 | $E''$ | 1D3 | TEMPERATURE | $K$ | Unary |
| POLCRY | $x_c$ | 0.0 | -- | -- | Unary |
| TGVK | $Tg$ | -- | TEMPERATURE | $K$ | Unary |
| TMVK | $Tm$ | -- | TEMPERATURE | $K$ | Unary |

# GLASS TRANSITION TEMPERATURE CORRELATION

The glass transition temperature model correlations are given below:

$$T_{g,j} = \sum n_{k,j} Y_{g,k} / \sum n_{k,j} M_{k,j}$$

$$T_g = \sum f_j M_j T_{g,j} / \sum f_j M_j$$

Where:

$T_{g,j}$ = $T_g$ for segment *j*

$Y_{g,k}$ = glass transition parameter for group *k*

$n_{k,j}$ = number of group *K* in segment *j*

$M_{k,j}$ = molecular weight of group *k* in segment *j*

$T_g$ = glass transition temperature for the polymer

$f_j$ = segment fraction of segment *j* in the polymer

$M_j$ = molecular weight of segment *j*

$Y_g$ values for functional groups are given in Appendix C.

## Glass Transition Correlation Parameters

The glass transition model parameters are given in Table 3.11.

***Table 3.11 Glass Transition Model Parameters***

| Parameter Name / Element | Symbol | Default | Units Keyword | Comments |
|---|---|---|---|---|
| TGVK | $T_g$ , or | ---- | TEMPERATURE | Unary |
| | $T_{g,j}$ | ---- | TEMPERATURE | Unary |

# MELT TRANSITION TEMPERATURE CORRELATION

The melt transition temperature model correlations are given below:

$$T_{m,j} = \sum n_{k,j} Y_{m,k} / \sum n_{k,j} M_{k,j}$$

$$T_m = \sum f_j M_j T_{m,j} / \sum f_j M_j$$

Where:

$T_{m,j}$ = $T_m$ for segment $j$

$Y_{m,k}$ = melt parameter for group $k$

$n_{k,j}$ = number of groups in segment $j$

$M_{k,j}$ = molecular weight of group $k$ in segment $j$

$T_m$ = melt temperature for the polymer

$f_j$ = fraction of segment $j$ in the polymer

$M_j$ = molecular weight of segment $j$

$Y_m$ values for functional groups are given in Appendix C.

## Melt Transition Model Parameters

The melt transition model parameters are given in Table 3.12.

***Table 3.12 Melt Temperature Model Parameters***

| Parameter Name / Element | Symbol | Default | Units Keyword | Comments |
|---|---|---|---|---|
| TMVK | $T_m$ , or | ---- | TEMPERATURE | Unary |
| | $T_{m,j}$ | ---- | TEMPERATURE | Unary |

# VAN KREVELEN PROPERTY PARAMETER ESTIMATION

Based on the group contribution concept, the van Krevelen models use the properties of functional groups to estimate heat capacity ( $Cp_l$, $Cp_c$ ), and density ( $\rho_l$, $\rho_c$, $\rho_g$ ), for polymer segments, and thereafter of polymers and oligomers.

In Polymers Plus, a polymer is defined in terms of its repeating units or segments. The van Krevelen models use the following approach to estimate properties for a system containing polymers:

1. First the segment properties are estimated using the properties of the functional groups which make up the segment(s). For example, for heat capacity, *Cp*, the segment property is calculated as the sum of the functional group values using:

   $$Cp = \sum_k n_k Cp_k$$

   Where subscript *k* refers to the functional group. Correlations for other properties are given in Appendix C.

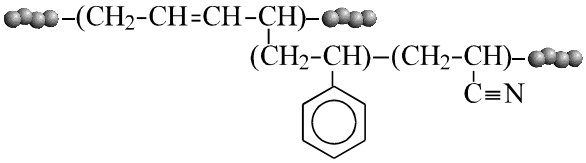
   If you are retrieving the segments from the SEGMENT databank, you do not need to supply functional groups. If you are not retrieving the segments from SEGMENT, or wish to override their databank functional group definition, you must supply their molecular structure in terms of van Krevelen functional groups.

2. Then the polymer properties are calculated using the properties of polymer segments, number average degree of polymerization, and segment composition.

3. Finally, mixture properties for the whole component system (polymer, monomer, and solvents) are calculated.

Table 3.13 shows an illustration of this approach for acrylonitrile-butadiene-styrene (ABS). The van Krevelen functional groups available in Polymers Plus are given in Appendix C.

***Table 3.13 Illustration of Functional Group Definition***

| Polymer | Segments | Functional Groups |
|---|---|---|
| ABS  | Butadiene-R<br>$-CH_2-CH=CH-CH<$ | $-CH_2-$<br>$-CH=CH$<br>$-CH<$ |
| | Styrene-R<br>$-CH_2-CH-$  | $-CH_2-$<br>$-CH<$  |
| | Acrylonitrile-R<br>$-CH_2-CH-$<br>$C\equiv N$ | $-CH_2-$<br>$-CH-$<br>$-C\equiv N$ |

# SPECIFYING PHYSICAL PROPERTIES

Following is an explanation of common procedures for working with physical properties.

## Selecting Physical Property Methods

For a Polymers Plus simulation, you must specify the physical property method(s) to be used. Polymers Plus provides many built-in property methods. You can either select one of these built-in property methods, or customize your own property method. Moreover, you can choose a property method for the entire flowsheet, part of a flowsheet or a unit.

**To select a built-in property method for the entire flowsheet:**

1. From the Data Browser, double click on the **Properties** folder.
2. From the **Properties** folder, go to the **Specifications** form.
3. On the **Specifications** global sheet, specify **Process type** and **Base method**.

You can also specify property methods for flowsheet sections.

Once you have chosen a built-in property method, the property routes and models used are resolved for you. You may use any number of property methods in a simulation.

## Creating Customized Physical Property Methods

Occasionally, you may prefer to construct new property methods customized for your own modeling needs.

### To create customized property methods:

1. From the Data Browser, find the **Properties** folder.
2. From the **Properties** folder, go to the **Property Methods** folder.

   An object manager appears.

   Click on **New**.
3. In the **Create new ID** dialog box, enter property method ID and click on **OK**.

Now you are ready to customize Routes and/or Models used in the property method you created. In general, to create a custom-made property method you select a base method and modify it.

### To customize routes the following steps are taken:

1. On the, **Routes** sheet, select a base method to be modified for customization.

   A **Property** versus **Route ID** table will automatically be filled depending upon your choice.
2. Click on the **Route ID** that is to be changed. From the list, select the new route ID.

If the customization procedure is properly completed, the new route ID will appear highlighted.

### To customize the models:

1. Click on the **Models** tab.
2. In the **Models** form, from the **Property** versus **Model name** table, click on the model name to be replaced and select the new model name from the list.

If the customization procedure is properly completed, the new model name will appear highlighted.

## Entering Parameters for a Physical Property Model

Frequently you need to enter pure model parameters for a pure-component or mixture physical property model.

### To enter pure model parameters:

1. From the Data Browser, open the **Properties** folder.
2. Several subfolders appear. Open the **Parameters** folder.

   The following folders appear:

   - Pure Component
   - Binary Interaction
   - Electrolyte Pair
   - Electrolyte Ternary
   - UNIFAC Group
   - UNIFAC Group Binary
   - Results

The following is a description of pure component parameter entry. Other parameter entries can be accomplished similarly.

### To enter component parameters:

1. Open the **Pure Component** folder.

   An object manager appears.

2. Click on **New**. A **New Pure Component Parameters** form appears.

The **New Pure Component Parameters** form is used to select the type of the pure component parameter. The selections are:

- Scalar (default)
- T-dependent correlation
- Nonconventional

### To prepare a New Pure Component Parameters form:

1. Select the type of the parameter (for example click **Scalar**).
2. On the same component parameter form, click on the name box and either enter a name, or accept the default, and click on **OK**.

Now the parameter form is ready for parameter entry.

### To enter a parameter:

1. Click on the **Parameters** box. From the list, chose the name of the parameter.
2. Click on the **Units** box. Enter the proper unit for the parameter.
3. Click on the **Component** column. Enter the parameter value.

The task is complete. Click on the **Next** button  to proceed.

## Entering a Physical Property Parameter Estimation Method

If a parameter value for a physical property model is missing, you can request property parameter estimation.

**To use parameter estimation:**

1. From the Data Browser, open the **Properties** folder.
2. Several subfolders appear. Open the **Estimation** folder. A **Setup** sheet appears.

There are three estimation options available in the **Setup** sheet:

- Do not estimate any parameters (default)
- Estimate all missing parameters
- Estimate only the selected parameters
  - Pure component scalar parameters
  - Pure component temperature-dependent property correlation parameters
  - Binary interaction parameters
  - UNIFAC group parameters

In the default option, no parameters are estimated during the simulation. If the second option is selected, then all missing parameters will be estimated according to a preset hierarchy of the Aspen Plus simulator. If you select either of these first two options, then the task is completed, and you can continue by clicking on the **Next** button  .

**If you select the option to estimate only selected parameters, then several more steps must be completed:**

1. In the object manager, click to select the **Estimate only the selected parameters** option. All parameter types will be selected automatically.
2. Check off all parameter types that you do *not* want estimated by clicking on the check marks in boxes by the parameter names.
3. Click on the parameter tab in the object manager for the parameters you want to estimate.
4. Fill in the parameter form by selecting the names of components, parameters, and estimation methods etc. from the lists.

The task is complete. Click on the **Next** button  to proceed.

## Entering Molecular Structure for a Physical Property Estimation

If a particular component is not in the component databank, or its structure is to be defined for a particular physical property estimation method, then you need to supply the molecular structure information. There are several ways to provide this information:

1. From the Data Browser, open the **Properties** folder.
2. Several subfolders appear. Click on the **Molecular Structure** folder. An object manager appears.
3. All the components selected for current simulation are listed in the object manager. Click on the name of the component structure which is to be entered. Click on **Edit**.

   A Molecular Structure Data Browser appears. Three options are available in the data-browser as forms for structure definition:

   - General (default form)
   - Functional group
   - Formula
4. Select the method you want to use and define the molecule according to the method selected.

The task is completed, you may proceed by clicking on the **Next** button  .

## Entering Data for Physical Properties Parameter Optimization

If data is available for a particular physical property, this data can be used to fit a property model available in Polymers Plus.

**In order to accomplish this data fit, first the data must be supplied to the system:**

1. From the Data Browser, open the **Properties** folder.
2. Click on the **Data** folder.

   An object manager appears.
3. Click on **New**. A **Create a new ID** form appears.

   Enter a name for the data form or accept the default.
4. In the same form, select the data type:

   - MIXTURE
   - PURE-COMP

   The following is a description for pure component data entry. Similar steps are required for mixture data entry.
5. Select a property from the **Property** drop down list.
6. Select a component from the **Component** drop down list.
7. Click on the **Data** tab.

   Enter the data in proper units.
8. Click on the **Next** button  to continue.

Note that the numbers in the first row in the data form indicate estimated standard deviation in each piece of data. They are automatically filled in, but you can edit those figures if necessary.

# REFERENCES

Van Krevelen, D. W., Properties of Polymers, 3rd Ed., Elsevier, Amsterdam (1990).

# 3.2 TAIT MOLAR VOLUME MODEL

This section describes the Tait property model available in Polymers Plus.

Topics covered include:

- Summary of Applicability
- Tait Molar Volume Model
- Specifying the Tait Molar Volume Model

## SUMMARY OF APPLICABILITY

The Tait molar volume model is an empirical correlation of the molar volume of polymer and oligomer components with temperature and pressure. This model is especially useful when the model parameters are available in the literature, or can be estimated through experimental data regression. Due to the empirical nature of the model, it should be used only within the ranges of temperature and pressure that were used to obtain the model parameters for each polymer or oligomer.

The Tait model is applicable over a wide range of temperature and pressure, and it is particularly useful in cases where the effect of pressure is significant. In almost all cases, the average error with the Tait model was found to be within the reported experimental error (approximately 0.1%).

# TAIT MOLAR VOLUME MODEL

The Tait equation is a P-V-T relationship for pure polymers which gives the best representation of P-V-T data for most polymers (Danner and High, 1992). This empirical equation uses a polynomial expression for the zero pressure isobar.

The Tait equation for polymers is used to calculate the molar volume of component *i* as follows:

$$V_i = Mw_n \times V_i(0,T)\left(1 - C\ln\left[1 + \frac{P}{B_i(T)}\right]\right) \quad \textbf{(3.21)}$$

$$V_i(0,T) = A_0 + A_1(T - 273.15) + A_2(T - 273.15)^2 \quad \textbf{(3.22)}$$

$$B_i(T) = B_0 \exp\left[-B_1(T - 273.15)\right] \quad \textbf{(3.23)}$$

Where:

$C$ = 0.0894

$V_i$ = molar volume in $m^3$ / *kgmole*

$V_i(0,T)$ = zero pressure isobar

$P$ = pressure in Pascals $\left(P_{lower} \le P \le P_{upper}\right)$

$T$ = temperature in Kelvin $\left(T_{lower} \le T \le T_{upper}\right)$

$Mw_n$ = polymer molecular weight

$A_0$, $A_1$, $A_2$, $B_0$, $B_1$ = specific constants

Values for several common polymers are given in Appendix D.

## Tait Model Parameters

The Tait model parameters are given in Table 3.14. These parameters may be entered on the T-Dependent correlation Input form located in the Pure Component subfolder.

***Table 3.14 Tait Model Parameters***

| Parameter Name / Element | Symbol | Default | Units Keyword | SI Units | Comments |
|---|---|---|---|---|---|
| VLTAIT/1 | $A_0$ | 1D35 | MASS-VOLUME, TEMPERATURE | $CUM / KG$ | Unary |
| VLTAIT/2 | $A_1$ | 1D35 | MASS-VOLUME, TEMPERATURE | $CUM / KG - K$ | Unary |
| VLTAIT/3 | $A_2$ | 1D35 | MASS-VOLUME, TEMPERATURE | $CUM / KG - K^2$ | Unary |
| VLTAIT/4 | $B_0$ | 1D35 | PRESSURE | $PASCALS$ | Unary |
| VLTAIT/5 | $B_1$ | 1D35 | TEMPERATURE | $K^{-1}$ | Unary |
| VLTAIT/6 | $P_{lower}$ | 0 | PRESSURE | $PASCALS$ | Unary |
| VLTAIT/7 | $P_{upper}$ | 1D35 | PRESSURE | $PASCALS$ | Unary |
| VLTAIT/8 | $T_{lower}$ | 0 | TEMPERATURE | $K$ | Unary |
| VLTAIT/9 | $T_{upper}$ | 1D3 | TEMPERATURE | $K$ | Unary |

# SPECIFYING THE TAIT MOLAR VOLUME MODEL

See Specifying Physical Properties in Section 3.1.

# REFERENCES

Danner R. P., and M. S. High, Handbook of Polymer Solution Thermodynamics, Design Institute for Physical Property Data, American Institute of Chemical Engineers (1992).

# 3.3 POLYMER VISCOSITY MODELS

This section describes the polymer viscosity models. Polymer melt viscosity is calculated using the Modified Mark-Houwink/Van Krevelen model. Concentrated polymer solution viscosity is calculated using the Van Krevelen mixture model.

Topics covered include:

- Summary of Applicability
- Pure Polymer Modified Mark-Houwink Model
- Concentrated Polymer Solution Viscosity Model
- Specifying the Viscosity Models

## SUMMARY OF APPLICABILITY

The modified Mark-Houwink/Van Krevelen model is used to calculate the zero-shear viscosity of polymer melts and polymer solutions. For polymer melts, the effects of temperature and polymer molecular weight on viscosity are considered. The model can be used correlatively (in the presence of viscosity data for regression) or in the predictive mode, as proposed by Van Krevelen. For polymer solutions, the effect of polymer concentration is also considered. The polymer solution viscosity model correlates the entire concentration range from pure polymer melt to polymer at infinite dilution with reasonable accuracy.

# PURE POLYMER MODIFIED MARK-HOUWINK MODEL

The polymer melt viscosity varies with the polymer structural characteristics, state conditions, and shear history. Currently, the melt viscosity model available in Polymers Plus considers the effects of polymer structure, polymer molecular weight and molecular weight averages, and temperature. This model combines two zero-shear viscosity correlations. The modified Mark-Houwink equation correlates polymer molecular weight and temperature effect; the Van Krevelen method estimates viscosity-temperature function based on functional group properties. The Andrade/DIPPR model is used to calculate viscosity for conventional components (Andrade, 1930).

Polymer melt viscosity increases as polymer molecular weight increases. The classical Mark-Houwink equation correlates the viscosity-molecular weight dependency with a power-law expression. Polymer melt viscosity is also a strong function of temperature; it decreases as the temperature increases. The Modified Mark-Houwink (MMH) equation uses an Arrhenius expression to account for the viscosity-temperature relationship:

*Modified Mark-Houwink Expression*

$$\eta_0 = \eta_{cr}\left(\frac{\overline{M}_w}{M_{cr}}\right)^{\alpha} \exp\left(E_\eta / RT^{\beta}\right) \qquad \textbf{(3.24)}$$

Where:

$\eta_0$ = zero-shear viscosity

$\eta_{cr}$ = zero-shear, critical mass viscosity

$\overline{M}_w$ = weight average molecular weight for polymers (MWW attribute or calculated using POLPDI)

$M_{cr}$ = critical molecular weight of polymer, at which viscosity-molecular weight dependency changes. It corresponds to the polymer weight-average molecular weight at the turning point of a $\log \eta_0$ vs. $\log \overline{M}_w$ plot (See Figure 3.5).

$\alpha$ = exponential factor accounting for the polymer molecular weight effect. This is a two parameter vector where

$\alpha(1)$ is used for $\overline{M}_w > M_{cr}$

$\alpha(2)$ is used for $\overline{M}_w \leq M_{cr}$

$E_\eta$ = activation energy of viscous flow

$R$ = universal gas constant

$T$ = absolute temperature

$\beta$ = empirical temperature exponent

The value for critical molecular weight is available for a limited number of POLYMER databank polymers (Van Krevelen, 1990). If the critical molecular weight for a polymer component is not available from the databank, it must be supplied by the user.

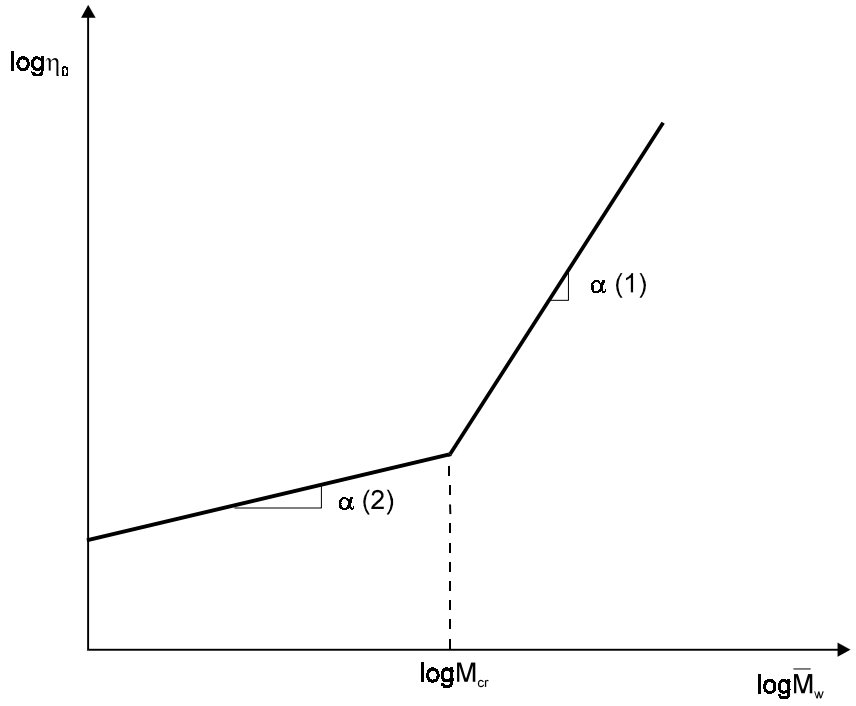



***Figure 3.5*** *Polymer Melt Viscosity vs. Molecular Weight*

## Modified Mark-Houwink Model Parameters

The parameters $E_\eta$, $\eta_{cr}$, and $\beta$ used in the MMH equation are related to the polymer structure, the others are related to polymer molecular weight. Values for $\eta_{cr}$, $E_\eta$ and $\beta$ can be regressed from experimental data and entered for any polymer or oligomer. Therefore, if viscosity-temperature data is available for a given polymer component, a Data Regression (DRS) simulation can be made to obtain the MMH equation parameters.

Note that in DRS runs, the polymer must be treated as an oligomer.

Table 3.15 lists the MMH model parameters.

***Table 3.15 Modified Mark-Houwink Model Parameters***

| Parameter Name / Element | Symbol | Default | Lower Limit | Upper Limit | Units Keyword | Comments |
|---|---|---|---|---|---|---|
| MULMH/1 | $\eta_{cr}$ | --- | 1.D-10 | 1.D10 | VISCOSITY | Unary |
| MULMH/2 | $E_\eta$ | 0D0 | 0D0 | 1D10 | MOLE-ENTHALPY | Unary |
| MULMH/3 | $\alpha(1)$ | 3.4 | 0D0 | 20.0 | --- | Unary |
| MULMH/4 | $\alpha(2)$ | 1.0 | 0D0 | 20.0 | --- | Unary |
| MULMH/5 | $\beta$ | 1.0 | 0.1 | 5.0 | --- | Unary |
| CRITMW | $M_{cr}$ | --- | 1.0 | 1D10 | -- | Unary |
| POLPDI* | $PDI$ | 1.0 | 1.0 | 1D4 | --- | Unary |
| TGVK** | $T_g$ | --- | --- | --- | TEMPERATURE | Unary |

* ***Only required for Data Regression (DRS) runs and for oligomer components.***

** ***By default, $T_g$ is calculated using the Van Krevelen group contribution method, unless it is provided by the user.***

## Van Krevelen Viscosity-Temperature Correlation

In Equation 3.24, if no MMH parameters are supplied the Arrhenius term drops out:

$$\eta_0 = \eta_{cr}(T)\left(\frac{\overline{M}_w}{M_{cr}}\right)^{\alpha} \quad \textbf{(3.25)}$$

In this case, the $\eta_{cr}(T)$ term is estimated using the Van Krevelen viscosity-temperature correlation.

The Van Krevelen viscosity-temperature correlation estimates the $\eta_{cr}$ based on polymer structural information and glass transition temperature. Figure 3.6 shows the viscosity-temperature relationship for a number of common polymer components. The zero-shear viscosity of various polymers exhibit similar $\eta - T$ trends. If $T \leq 1.2T_g$, all the polymers follow a Williams-Landel-Ferry (WLF) relationship (Williams et al., 1955). At higher temperatures, different polymers follow different paths.

Van Krevelen modeled this behavior using a group contribution method. The principles of the Van Krevelen method can be summarized as follows:

- The viscosity-temperature relationship of different polymer components can be represented by a number of master curves. These master curves are functions of three parameters: the polymer glass transition temperature $T_g$, the critical mass viscosity at $T = 1.2T_g\left[\eta_{cr}(1.2T_g)\right]$, and a structural parameter *A*.
- A new transport property called the viscosity-temperature gradient, $H_\eta$, is defined. Each functional group of a polymer molecule has a unique value for $H_\eta$ which is mole-additive with respect to functional groups and segments.
- $H_\eta$ is used to compute $\eta_{cr}(1.2T_g)$ and *A*.

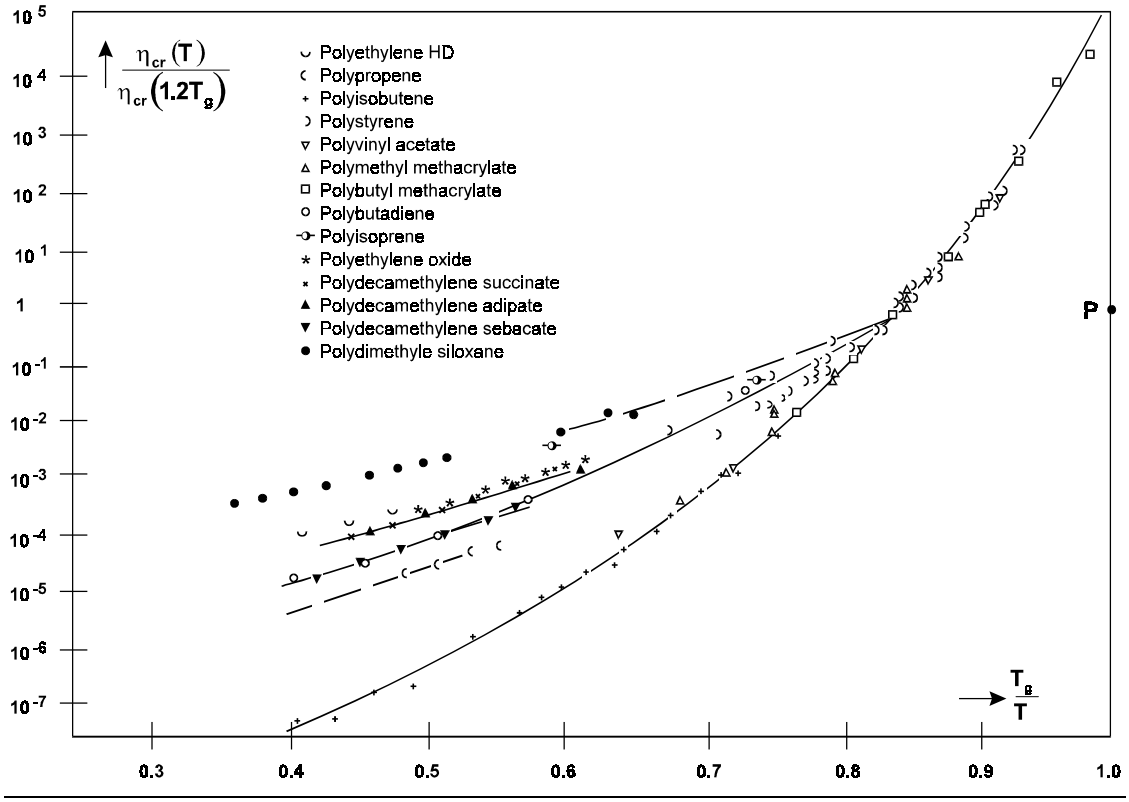



***Figure 3.6*** $\eta_{cr}$ *vs. T Graphical Correlation (Hoftyzer and Van Krevelen, 1976)*

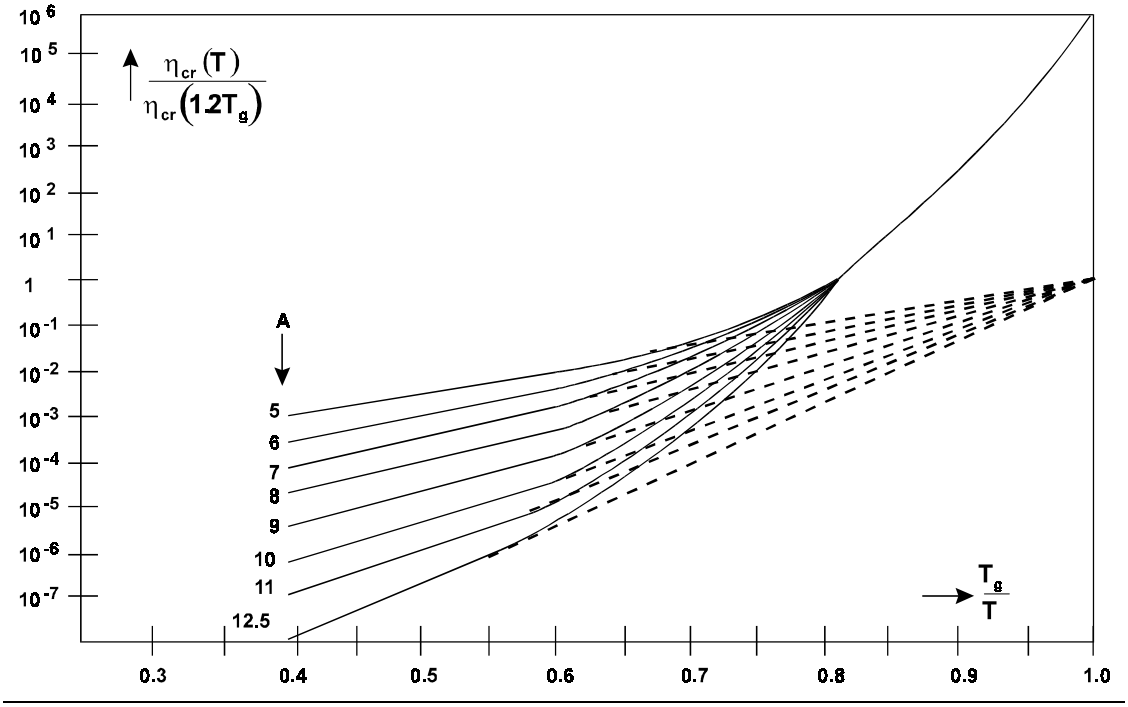



***Figure 3.7*** $\eta_{cr}$ *vs. T Master Curves (Hoftyzer and Van Krevelen, 1976)*

The Van Krevelen master curves which correlate the polymer viscosity-temperature relationship are shown in Figure 3.7. These master curves simulate the polymer viscosity-temperature behavior of Figure 3.6 in a graphical form. The Van Krevelen method calculates the critical mass viscosity at given temperature $\left[\eta_{cr}(T)\right]$, through the following steps:

1. Compute the component viscosity-temperature gradient from Van Krevelen functional group values. Polymers Plus uses the following mixing rules to compute polymer component viscosity-temperature gradient from Van Krevelen functional groups:

   for segments:

   $$H_{\eta j} = \sum_{k=1}^{Ngrp} n_{k,j} H_{\eta k,j} / M_j$$

   for polymers and oligomers:

   $$H_{\eta i} = \sum_{j=1}^{Ngrp} f_{ji} M_j H_{\eta j} / \sum_{j=1}^{Nseg} f_{ji} M_j$$

   Where:

   $H_{\eta j}$ = viscosity-temperature gradient of segment *j*

   $H_{\eta k,j}$ = viscosity-temperature gradient of group *k* in segment *j*

   $n_{kj}$ = number of occurrences of group *k* in segment *j*

   $H_{\eta i}$ = viscosity-temperature gradient of polymer *i*

   $f_{ji}$ = segment fraction (SFRAC) of segment *j* in polymer *i*

   $M_j$ = molecular weight of segment *j*

   *Ngrp* = number of types of groups in a segment

   *Nseg* = number of types of segments in a polymer

   $H_{\eta k,j}$ values for functional groups are given in Appendix C.

2. $E_\eta(\infty)$, the activation energy of viscous flow at high temperature is calculated from the polymer component viscosity-temperature gradient:

   $$E_\eta(\infty) = H_\eta^3$$

3. With $E_\eta(\infty)$ computed from group quantity, the following two parameters that affect polymer melt viscosity are estimated using the following equations:

The critical mass viscosity at $T = 1.2T_g$ is calculated using the WLF equation:

$$\log \eta_{cr}(1.2T_g) = E_\eta(\infty)\frac{(0.052 - 8.5 \times 10^{-5} T_g)}{T_g} - 1.4$$

The structural parameter *A* is calculated using the following equation:

$$A = \frac{1}{2.3}\frac{E_\eta(\infty)}{RT_g}$$

$T_g$ may be provided for polymer components. If $T_g$ is not supplied, the Van Krevelen estimate is used.

4. Given values for $T_g / T$ and *A*, the value for the reduced viscosity is obtained from the master curves shown on Figure 3.7 and where:

$$f\left(\frac{T_g}{T}, A\right) = \log\frac{\eta_{cr}(T)}{\eta_{cr}(1.2T_g)}$$

$\eta_{cr}(1.2T_g)$ is known from the previous step, therefore the final value for $\eta_{cr}(T)$ can be calculated.

## Van Krevelen Correlation Parameters

Among the Mark-Houwink model parameters described in Table 3.15, MULMH/3, MULMH/4, CRITMW, and TGVK are used in the Van Krevelen viscosity-temperature correlation.

# CONCENTRATED POLYMER SOLUTION VISCOSITY MODEL

The viscosity of concentrated polymer solutions exhibits characteristics similar to those of polymer melts. The influences of parameters such as molecular mass, temperature and shear rate on viscosity are largely similar. The viscosity of a polymer solution is also a function of polymer concentration. A discontinuity is observed in polymer solution viscosity vs. concentration profile at the so-called *critical concentration*. A solution is considered "concentrated" when the polymer weight concentration exceeds the critical concentration, typically at five percent by weight.

Historically, a clear distinction has been made in the literature between dilute polymer solutions and concentrated polymer solutions with regards to viscosity. In concentrated solutions, solvents reduce the solution viscosity by reducing the glass transition temperature, $T_g$, and through dilution effects. This model extends the Van Krevelen binary polymer solution viscosity correlations to multicomponent mixtures. The solution is treated as a quasi-binary mixture of polymer and solvent.

For mixtures without polymeric components, the Letsou-Stiel corresponding state correlation is used.

## Quasi-Binary System

The Van Krevelen binary polymer solution viscosity model in Polymers Plus treats a multicomponent polymer mixture as a quasi-binary system consisting of a pseudo-polymer component and a pseudo-solvent component. The pseudo-polymer component is a blend of all polymers and oligomers in the mixture which possesses properties averaged across the components present. The pseudo-solvent component is composed of all non-polymeric species present. The properties of the pseudo-solvent are averaged across the conventional species in the system.

## Properties of Pseudo-Components

A weight-average mixing rule is used to compute pseudopolymer properties:

$$Q^B = \sum_{i=1}^{Npol} w_i Q_{ip} \Big/ \sum_{i=1}^{Npol} w_i \qquad \textbf{(3.26)}$$

Where:

$Q^B$ = property of the pseudo-polymer (the superscript *B* stands for the pseudo-polymer)

*Npol* = total number of polymeric components in the system

$Q^B$ represents any of the following quantities:

$\eta_0^B$ = zero-shear viscosity of the pseudo-polymer. The above mixing rule for the pseudo-polymer viscosity is derived from the influence of polydispersity on zero-shear viscosity (Flory, 1943)

$H_\eta^B$ = Van Krevelen viscosity-temperature gradient of the pseudo-polymer. $H_\eta$ is additive for Van Krevelen groups, therefore, the viscosity-temperature gradient of the blend equals the weight-averaged viscosity-temperature gradient of all polymeric species

$T_g^B$ = glass transition temperature of the pseudo-polymer. Equation 3.26 is derived for $T_g^B$ by extending the Bueche formula to polymer mixtures, with an assumption that the *K* constant is the same for all polymers (Bueche, 1962)

$\gamma^B$ = power-law exponential factor which accounts for the real solvent dilution effects

$Q_{pi}$ = property of polymer component *i*, and represents any of the following quantities:

$\eta_{0i}$ = zero-shear viscosity of polymer *i*, computed from pure component viscosity models. It is a function of polymer molecular weight, temperature and polymer structure

$H_{\eta i}$ = Van Krevelen viscosity-temperature gradient of polymer *i*. It is estimated from the Van Krevelen group contribution method

$T_{gi}$ = glass transition temperature of polymer *i*. $T_g$ values are user specified or estimated from the Van Krevelen group contribution method

$\gamma_i$ = power-law exponent for solvent dilution of polymer *i*. $\gamma_i$ is correlated to the molecular weight exponential factor $\alpha$ discussed in Equation 3.25 by $\gamma / \alpha \approx 1.5$ usually varies between 4.0 to 5.6

The same mixing rule applies to the solvent mixture for the properties of the pseudo-solvent:

$$Q^S = \sum_{i=1}^{Nsol} w_i Q_{si} / \sum_{i=1}^{Nsol} w_i \qquad \textbf{(3.27)}$$

Where:

$Q^S$ = property of the pseudo-solvent (the superscript *S* stands for pseudo-component solvent)

*Nsol* = total number of solvent components in the system

$Q^S$ represents any of the following quantities:

$T_g^S$ = glass transition temperature of the pseudo-solvent component. The mixing rule for $T_g^S$ is an extension of the Bueche formula (Bueche 1962)

$K^S$ = constant related to the component volume expansion coefficient

$Q_{si}$ = property of solvent component *i* and represents any of the following quantities:

$T_{gi}$ = glass transition temperature of solvent component *i*. In situations when the solvent $T_g$ values are not available, user may use component melting point for estimation: $T_g \approx 2/3T_m$. $T_g$ values must be specified to for each solvent

$K_i$ = constant related to the component volume expansion coefficient:

$K_i \approx \dfrac{\alpha_{1s} - \alpha_{gs}}{\alpha_{1p} - \alpha_{gp}}$, $\alpha_1$ is the volume expansion coefficient above $T_g$, and $\alpha_g$ is the volume expansion coefficient below $T_g$. $K_i$ is defined as a solvent parameter. Typically, $K_i$ has values between 1.0 and 3.0. If there is no data available to estimate $K_i$, a default value of 2.5 is suggested

With the above mixing rules, the two pseudo-components properties needed to compute solution viscosity are available. The Van Krevelen binary solution model is applied to the quasi-binary solution to obtain the mixture

## Solution Viscosity Model Parameters

The parameters for the polymer mixture Van Krevelen viscosity model are listed in Table 3.16.

***Table 3.16 Polymer Mixture Van Krevelen Viscosity Model Parameter***

| Parameter Name / Element | Symbol | Default | Lower Limit | Upper Limit | Units Keyword | Comments |
|---|---|---|---|---|---|---|
| MULVK/1 | $K_i$ | 2.5 | 0D0 | 1D1 | --- | Unary |
| MULVK/2 | $\gamma_i$ | 5.1D0 | 1D0 | 1D1 | --- | Unary |
| TGVK | $T_g$ | --- | 0D0 | 5D3 | TEMPERATURE | Unary |

## Polymer Solution Viscosity Estimation

In a binary solution of polymer and solvent, the solution viscosity decreases as the solvent concentration increases. This is caused by a:

- Decrease of the viscosity of the pure polymer as a result of a decrease of the glass transition temperature
- Real dilution effect, which causes the viscosity of the solution to fall between that of the pure polymer and that of the pure solvent

For these reasons, the concentration dependency and temperature dependency of solution viscosity are strongly related. Polymer viscosity is much more significant than solvent viscosity. Therefore, in the Van Krevelen solution viscosity model, the solvent viscosity is neglected.

To calculate the binary polymer solution viscosity, the Van Krevelen model estimates $T_g$ of the polymer mixture, calculates the mixture viscosity at given temperature with the mixture glass point, then applies the true solvent dilution effect. The $T_g$ effect and the real dilution effect are imposed on the polymer viscosity only.

The polymer viscosity-temperature relationship is described in graphical form in the Van Krevelen polymer melt viscosity correlation in Figure 3.6. The steps used to calculate viscosity in the Van Krevelen solution viscosity model are illustrated in Figure 3.8.

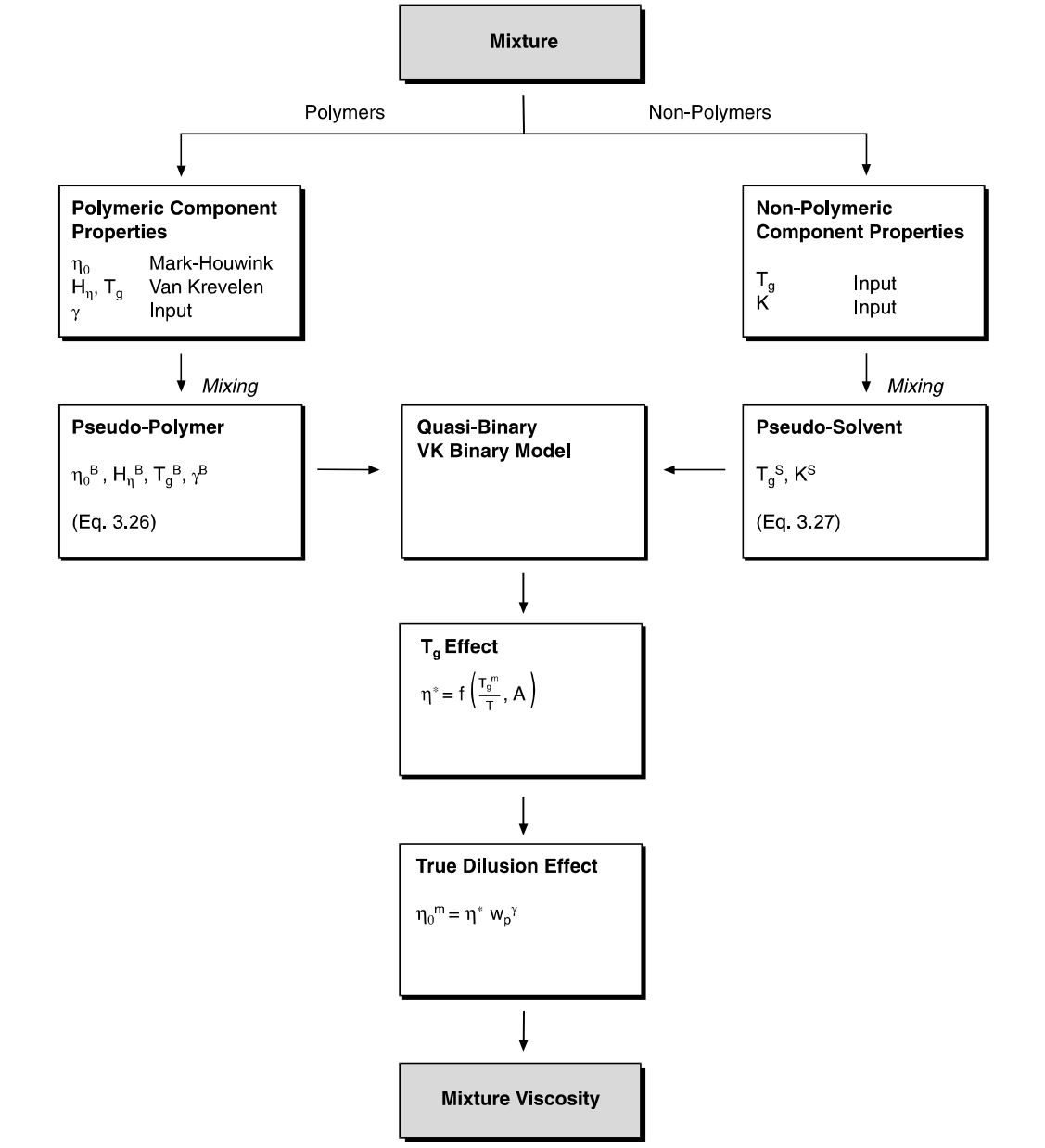



***Figure 3.8*** *Van Krevelen Solution Viscosity Model Structure*

## Polymer Solution Glass Transition Temperature

Polymer viscosity varies with glass transition temperature. Addition of a solvent to the polymer lowers the glass transition temperature to the mixture glass point $T_g^m$, and therefore lowers the polymer viscosity. This is the so-called plasticizer effect. A theoretical treatment of the plasticizer effect has been developed by Bueche who gave the following equation for the glass transition temperature of a plasticized polymer (Bueche, 1962):

$$T_g^m = \frac{T_g^B w_B + K^S T_g^S w_S}{w_B + K^S w_S} \quad \textbf{(3.28)}$$

Where:

$T_g^m$ = glass transition temperature of the mixture (superscript m stands for the mixture)

$w_B$ = total weight fraction of polymer in the mixture, $w_B = \sum_{i=1}^{Npol} w_i$

$w_S$ = total weight fraction of solvent in the mixture, $w_S = \sum_{i=1}^{Nsol} w_i$

## Polymer Viscosity At Mixture Glass Transition Temperature

For a polymer-solvent binary mixture, the undiluted polymer viscosity at the mixture glass point is calculated from the Van Krevelen viscosity-temperature relationship:

$$\log \frac{\eta^*}{\eta(1.2T_g)} = f\left(\frac{T_g^m}{T}, A\right) \quad \textbf{(3.29)}$$

Where:

$\eta^*$ = viscosity of the undiluted polymer with a new glass temperature

$\eta(1.2T_g)$ = viscosity of the undiluted polymer at its own glass temperature

$f$ = Van Krevelen graphical correlation for polymer melt viscosity

$A$ = structural factor related to the viscosity-temperature gradient of the polymer $H_\eta$ by:

$$A = \frac{(H_\eta)^3}{2.303RT_g} \quad \textbf{(3.30)}$$

For a quasi-binary system, the structural factor of pseudo-polymer, $A^B$, is used in Equation 3.29. $A^B$ is calculated using the pseudo-polymer properties:

$$\log\frac{\eta_B^*}{\eta^B\left(1.2T_g^B\right)} = f\left(\frac{T_g^m}{T}, A^B\right) \quad \textbf{(3.31)}$$

$$A^B = \frac{\left(H_\eta^B\right)^3}{2.303RT_g^B} \quad \textbf{(3.32)}$$

where $\eta^B(1.2T_g^B)$ is solved from the Van Krevelen zero shear viscosity graphical correlation of the pseudo-polymer $\eta_0^B$:

$$\log\frac{\eta_0^B}{\eta^B\left(1.2T_g^B\right)} = f\left(\frac{T_g^B}{T}, A^B\right) \quad \textbf{(3.33)}$$

## True Solvent Dilution Effect

The influence of the solvent concentration can be described by a power-law equation:

$$\eta_0^m = \eta^* w_p^{\gamma_p} \quad \textbf{(3.34)}$$

For a quasi-binary system, the mixture viscosity is:

$$\eta_0^m = \eta_B^* w_B^{\gamma_B} \quad \textbf{(3.35)}$$

Where:

$\eta_0^m$ = zero shear viscosity of the mixture

$\gamma_p$ = exponential factor that accounts for polymer concentration

$\gamma_B$ = exponential factor that accounts for the pseudo-polymer concentration

# SPECIFYING THE VISCOSITY MODELS

See Specifying Physical Properties in Section 3.1.

# REFERENCES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# 3.4 FLORY-HUGGINS ACTIVITY COEFFICIENT MODEL

This section describes the Flory-Huggins activity coefficient model. This model is used to calculate polymer and solvent activity coefficient and related physical properties such as fugacity coefficient, enthalpy, entropy, and free energy.

Topics covered include:

- Summary of Applicability
- Flory-Huggins Model
- Specifying the Flory-Huggins Model

## SUMMARY OF APPLICABILITY

The Flory-Huggins activity coefficient model gives good results if the interaction parameter $\chi$ is known accurately at the particular physical states of the system, i.e., temperature, composition, and polymer molecular weight. According to the Flory-Huggins theory the $\chi$ parameter should be independent of polymer concentration and of polymer molecular weight. In reality, it is shown to vary significantly with both.

The model works well if the interaction parameter at a low solvent concentration is used to estimate the activity coefficient at a higher solvent concentration. However, extrapolations to low solvent concentrations using $\chi$ based on a higher solvent concentration can lead to significant errors.

Finally, the Flory-Huggins model is not very accurate for polar systems, and unless it is used with a cubic-equation-of-state, it should not be used for phase equilibrium calculations at high pressures.

# FLORY-HUGGINS MODEL

Flory and Huggins independently derived an expression for the combinatorial entropy of mixing of polymer molecules with monomer molecules based on the lattice theory of fluids (Flory, 1941; Huggins, 1941). This statistical approach, widely used for liquid mixtures, takes into account the unequal size of the molecules and the linkage between flexible segments on the polymer chains. The enthalpy of mixing and the energetic interactions between the molecules are quantified through an interaction parameter $\chi$ for each molecule-molecule pair. (See Section 3.5 for a relationship of $\chi$ to NRTL interaction parameters.)

Consider a binary mixture with components differing significantly in molecular size: a polymer and a spherical solvent. To obtain the mixing properties of this system, Flory and Huggins applied lattice model to this system. The combinatorial and non-combinatorial properties of the mixture are derived by arranging both polymer and solvent on the lattice. Each solvent molecule occupies one lattice site. Each polymer molecule is divided into *m* flexible segments and each segment occupies one lattice site. Based on statistical arguments and several assumptions, the Gibbs free energy of mixing is derived as follows for a binary system:

$$\frac{\Delta G}{RT} = \left( \phi_1 \ln \phi_1 + \frac{\phi_2}{m} \ln \phi_2 + \chi_{12} \phi_1 \phi_2 \right) \left( n_1 + n_2 m \right) \qquad \textbf{(3.36)}$$

With:

$$\phi_1 = \frac{n_1}{n_1 + m n_2}$$

$$\phi_2 = \frac{m n_2}{n_1 + m n_2}$$

Where:

$\chi$ = molecular interaction parameter

$m$ = number of segments in the polymer molecule

$n_1$ = number of moles of solvent in the mixture

$n_2$ = number of polymer molecules in the mixture

$\phi_1$, $\phi_2$ = mole fractions on a segment basis

If *m* is set equal to the ratio of molar volumes of polymer and solvent, then $\phi_1$ and $\phi_2$ are the volume fractions.

If *m* is set equal to the ratio of molecular weight of polymer and solvent, then $\phi_1$ and $\phi_2$ are the weight fractions.

Therefore, Equation 3.36 is a generalized form that can be expanded to three different equations with $\phi$ being the segment-based mole fraction, volume fraction or weight fraction, depending on how *m* is defined. These three equations can be accessed in the Flory-Huggins model using option codes.

Option codes 1, 2, and 3, correspond to the weight basis, segment mole basis and volume basis, respectively. Option code 2 (segment basis) is the default.

A large portion of experimental polymer solution phase equilibria data in the open literature are reported using a volume fraction basis. The volume fraction basis allows users to directly apply interaction parameters from literature to their simulation. There are, however, situations where neither the segment-based mole fraction basis nor the volume fraction basis are appropriate. This is the case for many industrial processes of polymer mixtures. In such situations composition is usually known on a weight basis. Unlike segment mole fraction, component weight fraction remains consistent regardless of how the polymer segments are defined.

*Multicomponent Mixtures*

The derivation of Flory and Huggins has been extended to cover multiple components (Tompa, 1956):

$$\frac{\Delta G}{RT} = \left( \sum_i \frac{\phi_i}{m_i} \ln \phi_i + \sum_i \sum_{j<i} \chi_{ij} \phi_i \phi_j \right) \sum_i n_i m_i \qquad \textbf{(3.37)}$$

From Equation 3.37, one can derive the activity coefficient of a component:

$$\ln \gamma_i = \ln \frac{\phi_i}{x_i} + 1 - m_i \left( \sum_{j=1}^{n} \frac{\phi_j}{m_j} - \sum_{j=1}^{n} \phi_j \chi_{ij} + \sum_{j=1}^{n} \sum_{k>j}^{n} \chi_{jk} \phi_i \phi_j \right) \qquad \textbf{(3.38)}$$

Where:

$x_i$ = mole fraction of component *i*

For all three concentration basis, $m_i$ = the characteristic size of component *i*. It is related to the degree of polymerization by:

$$m_i = s_i * \overline{P}_i^{\varepsilon_i}$$

Where:

$P_i$ = degree of polymerization

$s_i$ and $\varepsilon_i$ = empirical parameters

$s_i$ and $\varepsilon_i$ account for deviation of the component characteristic size from its degree of polymerization. Users may use these parameters singly or in combination to adjust the component characteristic size. By default $P_i$ is 1.0 for small molecules.

The binary interaction parameter, $\chi_{ij}$ ,accounts for the enthalpic effects upon mixing. It is strongly dependent upon temperature:

*χ Parameter*

$$\chi_{ij} = \alpha_{ij} + \frac{\beta_{ij}}{T}$$

A summary of equations for the three concentration basis is given in Table 3.17.

### Table 3.17 Concentration Basis of Flory-Huggins Model

| Option | Description | Concentration | Characteristic Size |
|---|---|---|---|
| 1 | Mass Basis:<br>w = mass fraction<br>$M_n$ = number average mole weight for polymer/oligomer<br>mole weight for conventional component | $\phi_i = \frac{n_i \overline{M}_{n_i}}{\sum_j n_j \overline{M}_{n_j}} = w_i$ | $m_i = S_i * P_i^{t_i}$ |
| 2 | Segment mole fraction basis:<br>n = number of moles<br>P = number average chain length | $\phi_i = \frac{n_i \overline{P}_i}{\sum_j n_j \overline{P}_j}$ | $m_i = S_i * P_i^{t_i}$ |
| 3 | Volume basis:<br>V = molecular volume, $m^3$ / molecule<br>v = specific volume ( $m^3$ / kg )<br>w = mass fraction | $\phi_i = \frac{n_i V_i}{\sum_j n_j V_j} = \frac{w_i v_i}{\sum_j w_j v_j}$ | $m_i = S_i * P_i^{t_i}$ |

***For monomers,*** $P_n = POLDP = 1.0$ ***unless changed by the user.***

## Flory-Huggins Model Parameters

The input parameters for this model are given in Table 3.18. These parameters would normally be regressed from experimental data.

***Table 3.18 Flory-Huggins Model Parameters***

| Parameter Name / Element | Symbol | Default | Lower Limit | Upper Limit | Units | Comments |
|---|---|---|---|---|---|---|
| FHCHI/1 | $\alpha_{ij}$ | 0.0 | -1E2 | 1E2 | --- | Binary, symmetric |
| FHCHI/2 | $\beta_{ij}$ | 0.0 | -1E6 | 1E6 | --- | Binary, symmetric |
| FHSIZE/1 | $s_i$ | 1.0 | 0E0 | 1E15 | --- | Unary |
| FHSIZE/2 | $\varepsilon_I$ | 1.0 | -1E10 | 1E10 | --- | Unary |
| POLDP* | $P_i$ | 1.0 | --- | --- | --- | Unary |

* ***The actual degree of polymerization is used for polymer components.***

# SPECIFYING THE FLORY-HUGGINS MODEL

See Specifying Physical Properties in Section 3.1.

# REFERENCES

Flory, P. J., "Thermodynamics of High Polymer Solutions", *J. Chem. Phys*., **9**, 660 (1941).

Huggins, M. L., "Solutions of Long Chain Compounds", *J. Phys. Chem*., **9**, 440 (1941).

Tompa, H., Principles of Polymer Chemistry, Butterworths, London (1956).

# 3.5 NRTL ACTIVITY COEFFICIENT MODELS

This section describes Polymer Non-Random Two-Liquid activity coefficient models, the polymer NRTL model and the random copolymer NRTL model. Both models are based on the Non-Random concept extended to the segment approach. They differ primarily in the way pure copolymer state is defined. These models are used to calculate polymer and solvent activity coefficient and related physical properties such as fugacity coefficient, enthalpy, entropy, and free energy.

Topics covered include:

- Summary of Applicability
- Polymer NRTL Model Overview
- Random Copolymer NRTL Model
- Comparisons of the Polymer NRTL Models
- Specifying the Polymer NRTL Models

## SUMMARY OF APPLICABILITY

The polymer NRTL activity coefficient model is an extension of the NRTL model for low molecular weight compounds (Chen, 1993; Renon and Prausnitz, 1968). The main difference between this model and the Flory-Huggins model is that in the polymer NRTL activity coefficient model the binary interaction parameters are relatively independent of polymer concentration and polymer molecular weight. Furthermore, in the case of copolymers, the polymer NRTL binary parameters are independent of the relative composition of the repeat units on the polymer chain. This model can be used in a correlative mode at low and moderate pressures for a wide variety of fluids, including polar systems.

The current models do not address the free volume term or the so-called equation-of-state term, and strong orientational interactions, such as hydrogen bonding, as part of the entropy of mixing. As a result, the models cannot be used to represent lower critical solution temperature.

# POLYMER NRTL MODEL OVERVIEW

The polymer NRTL model and the random copolymer NRTL model are segment-based local composition models for the Gibbs energy of mixing of polymer solutions. These models represent a synergistic combination of the Flory-Huggins description for the entropy of mixing molecules of different sizes and the Non-Random Two Liquid theory for the enthalpy of mixing solvents and polymer segments. Both models reduce to the well-known NRTL equation if no polymers are present in the system.

The NRTL model is known to be one of the most widely used activity coefficient models. It has been used to represent phase behavior of systems with nonelectrolytes and electrolytes. The polymer NRTL model and the random copolymer NRTL model are extensions of the NRTL model from systems of small molecules to systems with both small molecules and macromolecules.

These models require the solvent-solvent, solvent-segment, and segment-segment binary parameters. The solvent-solvent binary parameters can be readily obtained from systems of monomeric molecules. Many such solvent-solvent binary parameters are available in the literature. Furthermore, the solvent-segment binary parameters have the desirable characteristic that they are relatively independent of temperature, chain length, and polymer concentration.

The polymer NRTL model and the random copolymer NRTL model provide flexible thermodynamic frameworks to correlate the phase behavior of polymer solutions. The models can be used to represent vapor-liquid equilibrium and liquid-liquid equilibrium of polymer systems.

# POLYMER NRTL MODEL

In the Polymer NRTL model, the Gibbs energy of mixing of a polymer solution is expressed as the sum of the entropy of mixing, based on the Flory-Huggins equation, and the enthalpy of mixing, based on the Non-Random Two Liquid theory.

The reference states for the polymer NRTL equation are pure liquids for solvents and a hypothetical segment aggregate state for polymers. In this hypothetical aggregate state, all segments are surrounded by segments of the same type. The following is the equation for the Gibbs energy of mixing:

$$\frac{\Delta G_{mixing}}{RT} = \frac{\Delta H_{mixing}^{NRTL}}{RT} - \frac{\Delta S_{mixing}^{FH}}{R}$$

$$\frac{\Delta G_{mixing}}{RT} = \Sigma_s n_s \frac{\Sigma_j x_j G_{js} \tau_{js}}{\Sigma_j x_j G_{js}} + n_p \Sigma_j r_{i,p} \frac{\Sigma_j x_j G_{ji} \tau_{ji}}{\Sigma_j x_j G_{ji}} + \Sigma_I n_I \ln \phi_I \qquad \textbf{(3.39)}$$

With:

$$x_i = \frac{X_I r_{i,I}}{\Sigma_J \Sigma_j X_J r_{j,J}}$$

$$G_{ji} = \exp(-\alpha_{ji} \tau_{ji})$$

$$\tau_{ji} = \frac{(g_{ji} - g_{ii})}{RT}$$

$$\phi_I = \frac{n_I m_I}{\Sigma_J n_J m_J}$$

Where:

| | | |
|---|---|---|
| $g_{ji}$ | = | energy of interaction between *j*-*i* pairs of species |
| $g_{ii}$ | = | energy of interaction between *i*-*i* pairs of species |
| $x_i$ | = | segment-based liquid phase mole fraction |
| $r_i$ | = | degree of polymerization |
| $n_I$ | = | number of moles |
| $m$ | = | ratio of polymer molar volume to segment molar volume |
| $\Phi$ | = | volume fraction (approximated as segment mole fraction) |
| $\tau$ | = | interaction parameter |
| $\alpha$ | = | NRTL non-randomness factor |
| *I* and *J* | = | component based indices |
| *i* and *j* | = | segment based indices |

The species *i* and *j* can be solvent molecules or segments.

The excess Gibbs energy expression is obtained by subtracting the ideal Gibbs energy of mixing from Equation 3.39:

$$\frac{\Delta G^{ex}}{RT} = \Sigma_s n_s \frac{\Sigma_j x_j G_{js} \tau_{js}}{\Sigma_j x_j G_{js}} + n_p \Sigma_i r_{i,p} \frac{\Sigma_j x_j G_{ji} \tau_{ji}}{\Sigma_j x_j G_{ji}} + \Sigma_I n_I \ln\left(\frac{\phi_I}{X_I}\right) \quad \textbf{(3.40)}$$

The activity coefficient of each species in the polymer solution can also be considered as the sum of two contributions:

$$\ln \gamma_I = \ln \gamma_I^{NRTL} + \ln \gamma_I^{FH}$$

With:

*Solvent Activity Coefficient*

$$\ln \gamma_{I=s}^{NRTL} = \frac{\Sigma_j x_j G_{js} \tau_{js}}{\Sigma_j x_k G_{ks}} + \Sigma_j \frac{x_j G_{js}}{\Sigma_k x_k G_{kj}} \left( \tau_{sj} - \frac{\Sigma_k x_k G_{kj} \tau_{kj}}{\Sigma_k x_k G_{kj}} \right) \quad \textbf{(3.41)}$$

*Polymer Activity Coefficient*

$$\ln \gamma_{I=p}^{NRTL} = \Sigma_i r_{i,p} \left[ \frac{\Sigma_j x_j G_{ji} \tau_{ji}}{\Sigma_k x_k G_{ki}} + \Sigma_j \frac{x_j G_{ji}}{\Sigma_k x_k G_{kj}} \left( \tau_{ij} - \frac{\Sigma_k x_k G_{kj} \tau_{kj}}{\Sigma_k x_k G_{kj}} \right) \right] \quad \textbf{(3.42)}$$

$$\ln \gamma_I^{FH} = \ln\left(\frac{\phi_I}{X_I}\right) + 1 - m_I \Sigma_J \left(\frac{\phi_J}{m_J}\right) \quad \textbf{(3.43)}$$

It is often useful for the case of homopolymers to establish a relationship between the NRTL interaction parameters and the Flory-Huggins $\chi_i$ parameter:

$$\chi_{ij} = \frac{\tau_{ji} G_{ji}}{\left(\phi_I + \phi_J G_{ji}\right)} + \frac{\tau_{ij} G_{ij}}{\left(\phi_J + \phi_I G_{ij}\right)} \quad \textbf{(3.44)}$$

Where:

$\chi_{ij}$ = solvent-polymer Flory-Huggins binary interaction parameter

# RANDOM COPOLYMER NRTL MODEL

The polymer NRTL model introduces the segment approach and applies the Non-Random concept to segment based species. The essence of the segment approach is to treat each segment type of a polymer molecule as an individual species.

In the polymer model, the NRTL formulation for local composition is applied to a polymer in the mixture state. It assumes a hypothetical segment aggregate state for the pure polymer.

In the random copolymer model, the NRTL formulation for local composition is applied to a polymer in a mixture and to the pure polymer.

The Gibbs energy of mixing, which is defined as the difference between the Gibbs energy of the mixture and that of the pure components, is equal to the sum of the entropy of mixing and the enthalpy of mixing. For the entropy of mixing, the Flory-Huggins theory is used:

$$\frac{\Delta S_{mixing}^{FH}}{R} = \Sigma_I n_I \ln \phi_I$$

For the enthalpy of mixing, the random copolymer NRTL model results in the following equation based on the non-random two-liquid segment approach:

$$\frac{\Delta H_{mixing}^{NRTL}}{RT} = \sum_I \sum_i \sum_j n_I r_{i,I} \tau_{ji} x_{ji} - \sum_I \sum_i \sum_j n_I r_{i,I} \tau_{ji} x_{ji}^{(I)} \quad \textbf{(3.45)}$$

The Gibbs energy of mixing of the system is equal to:

$$\frac{\Delta G_{mixing}}{RT} = \frac{\Delta H_{mixing}^{NRTL}}{RT} - \frac{\Delta S_{mixing}^{FH}}{R} = \sum_I \sum_i \sum_j n_I r_{i,I} \tau_{ji} x_{ji} - \sum_I \sum_i \sum_j n_I r_{i,I} \tau_{ji} x_{ji}^{(I)} + \sum_I n_I \ln \phi_I$$

**(3.46)**

With:

$$x_i = \frac{\sum_I X_I r_{i,I}}{\Sigma_J \Sigma_j X_J r_{j,J}}$$

$$x_{ji} = \frac{x_j G_{ji}}{x_i + \sum_{j \neq i} x_j G_{ji}}$$

$$x_{ji}^{(I)} = \frac{r_{j,I} G_{ji}}{r_{i,I} + \sum_{j \neq i} r_{j,I} G_{ji}}$$

$$\phi_I = \frac{n_I m_I}{\Sigma_J n_J m_J}$$

Where:

| | | |
|---|---|---|
| $x_i$ | = | segment based mole fraction for segment based species *i* |
| $g_{ji}$ | = | energies of interaction between *j*-*i* pairs of segment based species |
| $g_{ii}$ | = | energies of interaction between *i*-*i* pairs of segment based species |
| $r_{i,I}$ | = | number of segment type *i* in component *I* |
| $n_I$ | = | number of moles of component *I* |
| $\phi_I$ | = | volume fraction (approximated as segment mole fraction) |
| $\tau$ | = | interaction parameter |
| $X_I$ | = | mole fraction of *I* in component basis |
| $\alpha$ | = | NRTL non-random factor |
| *I* and *J* | = | component based indices |
| *i* and *j* | = | segment based indices |

The species *i* and *j* can be solvent molecules or segments.

The excess Gibbs energy expression is obtained by subtracting the ideal Gibbs energy of mixing from Equation 3.46:

$$\frac{\Delta G^{ex}}{RT} = \sum_I \sum_i \sum_j n_I r_{i,I} \tau_{ji} x_{ji} - \sum_I \sum_i \sum_j n_I r_{i,I} \tau_{ji} x_{ji}^{(I)} + \sum_I n_I \ln\left(\frac{\phi_I}{X_I}\right) \quad \textbf{(3.47)}$$

The activity coefficient of component *J* is obtained from the Gibbs energy of mixing as follows:

$$\ln \gamma_J = \ln \gamma_J^{\mathrm{NRTL}} + \ln \gamma_J^{\mathrm{FH}}$$

$$\ln \gamma_J^{NRTL} = \sum_i \frac{\sum_j r_{i,J} x_j G_{ji} \tau_{ji}}{\sum_k x_k G_{ki}} + \sum_i \frac{\sum_j x_i G_{ji}}{\sum_k x_k G_{ki}} \left( \tau_{ji} r_{j,J} - \frac{x_j \tau_{ji} \sum_k r_{k,J} G_{ki}}{\sum_k x_k G_{ki}} \right) - \sum_i \frac{\sum_j r_{i,J} r_{j,J} G_{ji} \tau_{ji}}{\sum_k r_{k,J} G_{ki}}$$

**(3.48)**

$$\ln \gamma_I^{FH} = \ln\left(\frac{\phi_I}{X_I}\right) + 1 - m_I \Sigma_J \left(\frac{\phi_J}{m_J}\right)$$

The random copolymer NRTL model reduces to the standard NRTL model for mixtures with no polymeric components. It reduces to the polymer NRTL model if the polymers present in a mixture are homopolymers, or if a copolymer mixture has zero interactions between the copolymer segments.

## Parameters for the NRTL Models

The polymer NRTL model and the random copolymer NRTL model have the same model parameters. They both require two binary interaction parameters, $\tau_{ij}$ and $\tau_{ji}$, for the solvent-solvent interactions, the solvent-segment interactions, and the segment-segment interactions. These binary interaction parameters become the correlation variables in representing the thermodynamic properties of polymer solutions. The binary interaction parameters have the following features:

- The models automatically retrieves the NRTL binary interaction parameters from the Aspen Plus databank for standard components when they are available.
- The binary parameters allow complex temperature dependence:

$$\tau_{ij} = a_{ij} + \frac{b_{ij}}{T} + e_{ij} \ln T + f_{ij} T \qquad \textbf{(3.49)}$$

- The non-randomness factor $\alpha_{ij}$ is allowed to be temperature dependent:

$$\alpha_{ij} = c_{ij} + d_{ij}(T - 273.15) \qquad \textbf{(3.50)}$$

  Typically, the temperature dependency is weak and $\alpha_{ij}$ is mainly influenced by $c_{ij}$. The default value for $c_{ij}$ is 0.3, and $\alpha_{ij}$ increases as the association between molecules increases.

The input parameters for the two models are summarized in Table 3.19. These parameters are normally regressed from experimental data.

***Table 3.19 Parameters for the Polymer NRTL Models***

| Parameter Name / Element | Symbol | Default | MDS | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|---|
| NRTL/1 | $a_{ij}$ | 0 | × | -100.0 | 100.0 | --- |
| NRTL/2 | $b_{ij}$ | 0 | × | -30000 | 30000 | TEMPERATURE |
| NRTL/3 | $c_{ij}$ | 0.3 | × | 0.0 | 1.0 | --- |
| NRTL/4 | $d_{ij}$ | 0 | × | -0.02 | 0.02 | TEMPERATURE |
| NRTL/5 | $e_{ij}$ | 0 | × | --- | --- | --- |
| NRTL/6 | $f_{ij}$ | 0 | × | --- | --- | 1/TEMPERATURE |

# COMPARISONS OF THE POLYMER NRTL MODELS

## Similarities

The polymer NRTL models have the following similarities:

- Both make use of the segment approach. The segments of a polymeric molecule are treated as individual species. The two-body interactions for segment-segment, solvent-segment and solvent-solvent pairs provide a detailed description of the molecular interactions in polymeric mixtures.
- The Non-Random Two-Liquid theory is used to describe the local compositions caused by the pair interactions between segment based species.
- The polymer NRTL model and the random copolymer NRTL model yield identical results for standard components and for homopolymers.

## Differences

The polymer NRTL models have the following differences:

- The excess Gibbs energy of a binary mixture is defined as:

  $$G^E = X_1(G^1_{mix} - G^1_{pure}) + X_2(G^2_{mix} - G^2_{pure})$$

  Both models use the segment based NRTL local composition formulation to calculate $G^I_{mix}$. When calculating $G^I_{pure}$, the polymer NRTL model assumes that the same type segments form a hypothetical aggregate, while the random copolymer NRTL model applies the NRTL theory to the segments. When the interaction between the same type of segments is strongly favored and causes the same type of segment aggregate together, the random copolymer NRTL model will yield the polymer NRTL model. The different treatments for pure polymer cause the models to behave differently for copolymer systems with non-zero interactions between the copolymer segments.

  For the treatment of copolymer in pure state, the polymer NRTL model is appropriate for block copolymers, the random copolymer NRTL model is appropriate for random copolymers.

# SPECIFYING THE POLYMER NRTL MODELS

See Specifying Physical Properties in Section 3.1.

# REFERENCES

Chen, C.-C., "A Segment-based Local Composition Model for the Gibbs Energy of Polymer Solutions," *Fluid Phase Equilibria*, **83**, 301-312 (1993).

Renon, H., and J. M. Prausnitz, “Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures”, *AIChE J.*, **14**, 135-144 (1968).

# 3.6 UNIFAC ACTIVITY COEFFICIENT MODEL

This section describes the UNIFAC activity coefficient model available in the POLYUF physical property method. This model is used to calculate monomer activity coefficient and related physical properties such as fugacity coefficient, enthalpy, entropy, and free energy.

Topics covered include:

- Summary of Applicability
- Polymer UNIFAC Model
- Specifying the UNIFAC Model

## SUMMARY OF APPLICABILITY

Polymer UNIFAC is an extension of the UNIFAC group contribution method for standard components to polymer systems (Fredenslund et al., 1975, 1977; Hansen et al., 1991). It is a predictive method of calculating phase equilibria, and therefore, it should be used only in the absence of experimental information. The UNIFAC method yields fairly accurate predictions. It becomes less reliable, however, in the dilute regions, especially for highly non-ideal systems (systems that exhibit strong association or solvation).

Although the UNIFAC approach is a good predictive method, it should not be used as a substitute to reducing good experimental data to calculate phase equilibria. In general, higher accuracy can be obtained from empirical models, when these models are used with binary interaction parameters obtained from experimental data.

Finally, the method is only applicable in the temperature range of 300-425 K (Danner and High, 1992). Extrapolation outside this range is not recommended. The group parameters are not temperature-dependent; consequently, predicted phase equilibria extrapolate poorly with respect to temperature.

# POLYMER UNIFAC MODEL

The polymer UNIFAC model calculates liquid activity coefficients for the POLYUF property method. This UNIFAC model is the same as the UNIFAC model in Aspen Plus for monomer systems except that this model obtains functional group information from segments and polymer component attributes.

The equation for the original UNIFAC liquid activity coefficient model is made up of a combinatorial and residual term:

$$\ln\gamma = \ln\gamma_i^C + \ln\gamma_i^R \quad \textbf{(3.51)}$$

$$\ln\gamma_i^C = \ln\frac{\phi_i}{x_i} + 1 - \frac{\phi_i}{x_i} - \frac{z}{2}\left(\ln\frac{\phi_i}{\theta_i} + 1 - \frac{\phi_i}{\theta_i}\right) \quad \textbf{(3.52)}$$

Where the molecular volume and surface fractions are:

$$\phi_i = \frac{x_i r_i}{\sum_j^{nc} x_j r_j} \text{ and } \theta_i = \frac{x_i \frac{z}{2} q_i}{\sum_j^{nc} x_j \frac{z}{2} q_j} \quad \textbf{(3.53)}$$

With:

*nc* = number of components in the mixture

The coordination number *z* is set to 10.

The parameters $r_i$ and $q_i$ are calculated from the group volume and area parameters:

$$r_i = \sum_k^{ng} \nu_{ki} R_k \text{ and } q_i = \sum_k^{ng} \nu_{ki} Q_k \quad \textbf{(3.54)}$$

Where:

$\nu_{ki}$ = number of groups of type *k* in molecule *i*

*ng* = number of groups in the mixture

The residual term is:

$$\ln\gamma_i^R = \sum_k^{ng} \nu_{ki}\left[\ln\Gamma_k - \ln\Gamma_k^i\right] \quad \textbf{(3.55)}$$

Where:

$\ln \Gamma_k$ = activity coefficient of a group at mixture composition

$\Gamma_k^i$ = activity coefficient of group *k* in a mixture of groups corresponding to pure *i*

The parameters $\Gamma_k$ and $\Gamma_k^i$ are defined by:

$$\ln \Gamma_k = Q_k \left( 1 - \ln \sum_m^{ng} \theta_m \tau_{mk} - \sum_m^{ng} \left( \frac{\theta_m \tau_{km}}{\sum_n^{ng} \theta_n \tau_{nm}} \right) \right) \quad \textbf{(3.56)}$$

With:

$$\theta_k = \frac{X_k \frac{z}{2} Q_k}{\sum_m^{ng} X_m \frac{z}{2} Q_m} \quad \textbf{(3.57)}$$

And:

$$\tau_{mn} = e^{-b_{mn}/T} \quad \textbf{(3.58)}$$

The parameter $X_k$ is the group mole fraction of group *k* in the liquid:

$$X_k = \frac{\sum_j^{nc} \nu_{kj} x_j}{\sum_j^{nc} \sum_m^{ng} \nu_{mj} x_j} \quad \textbf{(3.59)}$$

## Polymer UNIFAC Model Parameters

The input parameters for this model are given in Table 3.20.

***Table 3.20 Polymer UNIFAC Model Parameters***

| Parameter Name / Element | Symbol | Default | Lower Limit | Upper Limit | Units |
|---|---|---|---|---|---|
| UFGRP | $(\nu_{ki}, \nu_{mi},...)$ | --- | --- | --- | --- |
| GMUFQ | $Q_k$ | --- | --- | --- | --- |
| GMUFR | $R_k$ | --- | --- | --- | --- |
| GMUFB | $b_{kn}$ | --- | --- | --- | --- |

The parameter UFGRP stores the UNIFAC functional group number and number of occurrences of each group. UFGRP is stored in the Polymers Plus segment databank for polymer segments, and in the Aspen Plus pure component databank for standard components. For non-databank components, enter UFGRP on the Properties Molec-Struct.Func-Group form.

See *Aspen Plus Physical Property Methods and Models,* for a list of the UNIFAC functional groups.

# SPECIFYING THE UNIFAC MODEL

See Specifying Physical Properties in Section 3.1.

# REFERENCES


Aspen Plus Reference Manual, "Physical Property Methods and Models," Aspen Technology, Inc. (1998).

Danner R. P., and M. S. High, Handbook of Polymer Solution Thermodynamics, Design Institute for Physical Property Data, American Institute of Chemical Engineers (1992).

Fredenslund, Aa., R. L. Jones and J. M. Prausnitz, *AIChE J.*, **21**, 1086 (1975).

Fredenslund, Aa., J. Gmehling and P. Rasmussen, Vapor-Liquid Equilibria using UNIFAC, Amsterdam, Elsevier (1977).

Hansen, H. K., P. Rasmussen, Aa. Fredenslund, M. Schiller, and J. Gmehling, "Vapor-Liquid Equilibria by UNIFAC Group Contribution. 5 Revision and Extension," *Ind. Eng. Chem. Res.*, **30**, 2352-2355 (1991).

# 3.7 POLYMER UNIFAC FREE VOLUME MODEL

This section describes the UNIFAC free volume activity coefficient model available in the POLYUFV physical property method. This model is used to calculate monomer activity coefficient and related physical properties such as fugacity coefficient, enthalpy, entropy, and free energy.

Topics covered include:

- Summary of Applicability
- Polymer UNIFAC Free Volume Model
- Specifying the Polymer UNIFAC Free Volume Model

## SUMMARY OF APPLICABILITY

The UNIFAC free volume activity coefficient model is the same as the polymer UNIFAC model, with the exception that it contains a term to account for free-volume (compressibility) effects. Thus, the two methods have similar applicabilities (see Polymer UNIFAC Method). The UNIFAC-FV model can be used with more confidence for predictions at higher pressures than the polymer UNIFAC model. Nonetheless, both methods are predictive, and should not be used to substitute correlative models (such as Flory-Huggins or POLYNRTL) with fitted binary parameters.

# POLYMER UNIFAC FREE VOLUME MODEL

Oishi and Prausnitz (1978) modified the UNIFAC model (Fredenslund et al., 1975, 1977) to include "a contribution for free volume difference between the polymer and solvent molecules." Oishi and Prausnitz suggested that the UNIFAC combinatorial contribution does not account for the free volume differences between the polymer and solvent molecules. While this difference is usually not significant for small molecules, it could be important for polymer-solvent systems. They added the free volume contribution derived from the Flory equation of state to the original UNIFAC model to arrive at the following expression for the weight fraction activity coefficient of a solvent in a polymer:

$$\ln\gamma_i = \ln\gamma_i^C + \ln\gamma_i^R + \ln\gamma_i^{FV} \quad \textbf{(3.60)}$$

$$\ln\gamma_i^C = \ln\frac{\phi_i}{x_i} + 1 - \frac{\phi_i}{x_i} - \frac{z}{2}\left(\ln\frac{\phi_i}{\theta_i} + 1 - \frac{\phi_i}{\theta_i}\right) \quad \textbf{(3.61)}$$

$$\ln\gamma_i^R = \sum_k^{ng} \nu_{ki}\left[\ln\Gamma_k - \ln\Gamma_k^i\right] \quad \textbf{(3.62)}$$

*Free-Volume Contribution*

$$\ln\gamma_i^{FV} = 3C_i \ln\left[\frac{\tilde{V}_i^{\frac{1}{3}} - 1}{\tilde{V}_m^{\frac{1}{3}} - 1}\right] - C_i\left[\left(\frac{\tilde{V}_i}{\tilde{V}_m} - 1\right)\left(1 - \tilde{V}_i^{\frac{1}{3}}\right)^{-1}\right] \quad \textbf{(3.63)}$$

$$\tilde{V}_i = \frac{V_i}{0.01517 b r_i} \quad \textbf{(3.64)}$$

$$\tilde{V}_m = \frac{\sum V_i x_i}{0.01517 b \sum r_i x_i} \quad \textbf{(3.65)}$$

Where:

$C_i$ = 1.1

$b_i$ = 1.28

$r$ = volume parameter for component *i*

$V_i$ = specific volume of component *i*, cubic meters per kilogram mole, calculated from Rackett equation for segments and from Tait equation for polymers.

See Section 3.2 for a description of the Tait model.

The combinatorial and residual contributions $\gamma^C$ and $\gamma^R$ are identical to the polymer UNIFAC model (See Section 3.6).

The Oishi-Prausnitz modification of UNIFAC is currently the most used method available to predict solvent activities in polymers. Required for the Oishi-Prausnitz method are the densities of the pure solvent and pure polymer at the temperature of the mixture and the structure of the solvent and polymer. The Tait equation is used to calculate molar volume for polymers (See Section 3.2).

Molecules that can be constructed from the groups available in the UNIFAC method can be treated. At present, groups are available to construct alkanes, alkenes, alkynes, aromatics, water, alcohols, ketones, aldehydes, esters, ethers, amines, carboxylic acids, chlorinated compounds, brominated compounds, and a few other groups for specific molecules. The Oishi-Prausnitz method has been tested only for the simplest of these structures, and these groups should be used with care.

## Polymer UNIFAC Free Volume Model Parameters

The UNIFAC free volume parameters are the same as those required for the polymer UNIFAC model (See Section 3.6). In addition, parameters for the Tait molar volume model are required for free volume calculations (See Section 3.2).

# SPECIFYING THE POLYMER UNIFAC FREE VOLUME MODEL

See Specifying Physical Properties in Section 3.1.

# REFERENCES

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# 3.8 POLYMER IDEAL GAS PROPERTY MODEL

This section describes the ideal-gas model used in Polymers Plus. The model performs calculations for ideal-gas enthalpy, entropy, and heat capacity for polymers and oligomers. The ideal gas calculations are needed for use with the polymer equation of state models.

Topics covered include:

- Summary of Applicability
- Polymer Ideal Gas Property Model
- Specifying the Ideal Gas Model

## SUMMARY OF APPLICABILITY

Equations of state provide information concerning ideal gas *departure functions* (e.g., enthalpy departure $\Delta H$, entropy departure $\Delta S$, Gibbs free energy departure $\Delta G$) (Reid et al., 1987). In estimating enthalpy, entropy, and Gibbs free energy with an equation of state, the ideal gas contribution must be added to the departure functions obtained from the equation of state. The ideal gas model already available in Aspen Plus for monomers and solvents is extended to handle polymers and oligomers.

# POLYMER IDEAL GAS PROPERTY MODEL

The ideal gas enthalpy of a polymer at temperature $T$ is given by the following equation:

$$H^o_{pol}(T) = \Delta H^o_f(IG,298K) + \int_{298K}^{T} Cp^o(T)dT \qquad \textbf{(3.66)}$$

Where:

$\Delta H^o_f(IG,298K)$ = enthalpy of formation of the polymer at the ideal-gas state and 298K

$Cp^o(T)$ = ideal-gas heat capacity of the polymer

The quantity $\Delta H^o_f(IG,298K)$ is calculated for polymers and oligomers using the van Krevelen method (See Section 3.1).

In the case of copolymers, the enthalpy of formation is calculated for the segments using the van Krevelen approach, and then $\Delta H^o_f(IG,298K)$ for the copolymer is evaluated as a weighted average of the segment heat of formation:

$$\Delta H^o_f(IG,298K) = \left[\sum_k^{Nseg} SFRAC_k \Delta H^o_{f,k}\right] F \qquad \textbf{(3.67)}$$

With:

$$F = \frac{Mw_{pol}}{\sum_k^{Nseg} SFRAC_k\, Mw_k}$$

Where:

$\Delta H^o_{f,k}$ = ideal-gas enthalpy of formation of segment $k$

$F$ = molecular weight correction

$Mw_{pol}$ = reference molecular weight of the polymer

$Mw_k$ = molecular weight of the segment

Ideal-gas heat capacities are also calculated using a similar approach:

$$C_p^o = \left[ \sum_k^{Nseg} SFRAC_k C_{p,k}^o \right] F \qquad \textbf{(3.68)}$$

With:

$$Cp_k^o = C_{1k} + C_{2k}T + C_{3k}T^2 + C_{4k}T^3 + C_{5k}T^4 + C_{6k}T^5 \text{ for } C_{7k} \le T \le C_{8k} \qquad \textbf{(3.69)}$$

$$Cp_k^o = C_{9k} + C_{10k}T^{C_{11k}} \text{ for } T \le C_{7k} \qquad \textbf{(3.70)}$$

Where:

$Cp_k^o$ = ideal-gas heat capacity of the segment

$Cp_k^o$ = linearly extrapolated using slope at $C_{8k}$ for $T > C_{8k}$ (See *Aspen Plus Physical Property Methods and Models*).

The ideal gas entropy for polymers and oligomers is evaluated as follows:

$$S_{pol}^o(T) = \Delta S_f^o(IG,298K) + \int_{298K}^{T} \frac{Cp^o(T)}{T} dT \qquad \textbf{(3.71)}$$

With:

$$\Delta S_f^o(IG,298K) = \frac{\Delta H_f^o(IG,298K) - \Delta G_f^o(IG,298K)}{298K} \qquad \textbf{(3.72)}$$

Where:

$\Delta G_f^o(IG,298K)$ = Gibbs free energy of formation at ideal-gas conditions

In the case of polymers and oligomers, $\Delta G_f^o(IG,298K)$ is calculated using an expression similar to that for the ideal-gas enthalpy of formation:

$$\Delta G_f^o(IG,298K) = \left[ \sum_k^{Nseg} SFRAC_k \Delta G_{f,k}^o \right] F \qquad \textbf{(3.73)}$$

Where:

$\Delta G_{f,k}^o$ = ideal-gas Gibbs free energy of formation of segment *k*

## Polymer Ideal Gas Model Parameters

The parameters used in the ideal gas model are listed in Table 3.21. For polymers and oligomers using databank segments, these parameters are automatically calculated.

For components using non-databank segments, the parameters must be estimated. See Section 3.3 for descriptions on the approach used for parameter estimation.

***Table 3.21 Ideal Gas Model Parameters***

| Parameter Name / Element | Symbol | Default | Lower Limit | Upper Limit | Units Keyword | Comments |
|---|---|---|---|---|---|---|
| CPIG/1 | $C_{1k}$ | --- | --- | --- | MOLE-HEAT-CAPACITY, TEMP | Unary |
| CPIG/1,..., 6 | $C_{2k},...,C_{6k}$ | 0.0 | --- | --- | MOLE-HEAT-CAPACITY, TEMP | Unary |
| CPIG/7 | $C_{7k}$ | 0.0 | --- | --- | TEMP | Unary |
| CPIG/8 | $C_{8k}$ | D3 | --- | --- | TEMP | Unary |
| CPIG/9, 10, 11 | $C_{9k}, C_{10k}, C_{11k}$ | --- | --- | --- | MOLE-HEAT-CAPACITY, TEMP | Unary |
| DHFVK | $\Delta H^o_{f,k}$ | --- | --- | --- | MOLE-ENTHALPY | Unary |
| DGFVK | $\Delta G^o_{f,k}$ | --- | --- | --- | MOLE-ENTHALPY | Unary |

# SPECIFYING THE IDEAL GAS MODEL

See Specifying Physical Properties in Section 3.1.

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# 3.9 SANCHEZ-LACOMBE EOS MODEL

This section describes the Sanchez-Lacombe equation-of-state (EOS) model for polymers and polymer solutions. EOS models are used to calculate molar volumes, fugacity coefficients, heat capacities, and enthalpy, entropy, and Gibbs free energy departures, for both pure components and mixtures.

Topics covered include:

- Summary of Applicability
- Sanchez-Lacombe Model
- Specifying the Sanchez-Lacombe EOS Model

## SUMMARY OF APPLICABILITY

Activity coefficient models such as Flory-Huggins, NRTL, and UNIFAC, are used widely in industry mainly because of their simplicity. However, they suffer several important shortcomings:

- They are applicable only to incompressible liquid solutions, since they assume that there is no excess volume of mixing.
- They also fail to predict the Lower Critical Solution Temperature (LCST) type phase behavior.

  At the LCST, a phase separation of a polymer/solvent mixture is observed upon increasing the temperature, usually near the critical temperature of the solvent. The main reason for the phase split in LCST systems is the free-volume or density dissimilarities between the solvent and the polymer. As the critical point of the solvent is approached at a moderate pressure, the solvent molecules tend to take a more expanded gas-like configuration, resulting in a rapid drop in density with increasing temperature.

The polymer density, however, is still far from its hypothetical critical density. Therefore, the polymer does not undergo such a dilation effect with increasing temperature. This growing difference in density between the polymer and the solvent results in a phase separation.

- Activity coefficient models are inconsistent in the critical region
- Activity coefficient models are strictly mixture models, thus providing no information about the pure components.
- Activity coefficient models currently available in Polymers Plus assume that the polymer is entirely in the liquid phase, while ignoring the possible presence of small amount of polymer in the vapor phase.

In contrast to activity coefficient models, equations of state (EOS) do not suffer these shortcomings. EOS are able to predict both UCST (Upper Critical Solution Temperature) and LCST types of phase behavior in polymer solutions. EOS models are valid over the entire fluid region, from the dilute-gas to the dense-liquid region, and therefore, are not limited to incompressible liquids. Thus, unlike activity coefficient models, EOS are able to evaluate the physical properties of any fluid phase, liquid and/or vapor, such as fugacity, molar volume, enthalpy, entropy, and Gibbs free energy departure. In addition, EOS are able to account for possible presence of polymer in the gaseous phase. Finally, EOS are developed as pure-component models and subsequently extended to mixtures, thus providing information for both pure components and mixtures.

There is a large number of equations of state for polymer solutions in the literature, which can be classified in the following categories:

- Cell models
- Lattice models
- Hole models
- Tangent sphere models

*Cell Models*

In *cell models* for pure chain-like fluids, the system contains $N$ molecules each composed of $r$ segments arranged on a lattice having a total of $rN$ sites. One chain molecule occupies $r$ neighboring lattice sites. *Compressibility* or *free-volume* effects are introduced to the cell model with the fact that the cell volume increases with rising temperature. The most popular cell models are the EOS developed by Prigogine (Prigogine et al., 1953) and Flory-Orwoll-Vrij (Flory et al., 1964). These cell models illustrate a common feature of most EOS for chain fluids: three-parameter corresponding states in which the properties of pure fluids are described by a segment pair interaction energy, a segment volume, and a characteristic number of segments per molecules.

*Lattice Models*

*Lattice models*, like cell models, also are based on the incompressible lattice theory. The difference between cell and lattice models is in the way they account for free-volume effects. Lattice models assume that the lattice is occupied by both chains and vacant lattice sites or holes. Thus, a pure chain fluid is treated as a binary mixture between molecules and holes.

The EOS proposed by Sanchez and Lacombe (Lacombe and Sanchez, 1976) is the most used and the most representative of lattice equations of state. Others include the Costas-Sanctuary EOS, which accounts for chain connectivity through a *surface area* parameter, the Panayiotou-Vera EOS, which utilizes the quasi-chemical approach to account for non-random mixing of chains and holes, and the Mean-Field Lattice-Gas EOS, proposed by Kleintjens and Koningsveld ( Costas et al, 1981; Panayiotou et al, 1982; Koningsveld et al, 1987).

*Hole Models*

*Hole models* represent a combination of two approaches for incorporating free-volume effects into the lattice model. In particular, the lattice has vacant sites and, at the same time, the cell volume is variable. One such equation of state is the Simha-Somcynsky EOS (Simha and Somcynsky, 1969), which also represents a three-parameter corresponding states theory.

*Tangent-sphere Models*

*Tangent-sphere models*, treat molecules as a chain of freely-jointed, tangent hard spheres, where segments on a chain are tangent with their neighboring segments, and can rotate freely without overlaps. Recent advances in statistical mechanics have shown that the thermodynamic properties of chain molecules can be written in the general form:

$$\Theta = \Theta^{ref} + \Theta^{pert}$$

Where:

| | | |
|---|---|---|
| $\Theta$ | = | any thermodynamic property (pressure, free energy, etc.) |
| $\Theta^{ref}$ | = | property of a reference fluid |
| $\Theta^{pert}$ | = | contribution to the property $\Theta$ of the *perturbation* term, the difference between the total and the reference property of the fluid |

Characteristic representatives of this class of theories are the *perturbed-hard chain theory* (PHCT), the *generalized Flory theory* (GF), and the *statistical associated fluid theory* (SAFT).

PHCT was developed by Prausnitz and coworkers (Donohue and Prausnitz, 1978), and represents the first attempt to combine the vast body of knowledge in statistical mechanics into a practical equation of state for industrial applications. The GF theories were developed by Hall and coworkers (Dickman and Hall, 1986; Yethiraj and Hall, 1991). The starting point of the GF models is Flory's estimate for the probability of inserting an r-mer molecule into a sea of r-mers on a lattice. Hall rigorously extended this insertion probability, which is related to the thermodynamic pressure, to the continuous-space fluid. SAFT was developed by Chapman, Gubbins, Radosz, and collaborators based on extensions and simplifications of a theory due to Wertheim (Chapman et al, 1989; Huang and Radosz, 1990, 1991; Wertheim, 1984, 1986). SAFT uses a different reference fluid than GF and PHCT. In SAFT, the reference term accounts also for chemical association or hydrogen-bonding. SAFT EOS has been applied recently for phase equilibrium calculations of polymer systems with promising results.

# SANCHEZ-LACOMBE MODEL

## Pure Fluids

According to the lattice theory of Sanchez and Lacombe, a pure fluid is viewed as a mixture of molecules and holes, confined on the sites of a lattice (Sanchez and Lacombe, 1976). Each segment of the chain, as well as each hole, occupies one lattice site. The total number of lattice sites for a binary mixture of $N$ r-mers and $N_0$ empty sites is:

$$N_r = N_0 + rN \tag{3.74}$$

The total volume of the system is:

$$V = \left(N_0 + rN\right)v^* \tag{3.75}$$

Where:

$v^*$ = volume of a lattice site

Sanchez and Lacombe defined a reduced density as the fraction of occupied lattice sites:

$$\tilde{\rho} = \frac{\rho^*}{\rho} = \frac{rN}{N_0 + rN} \tag{3.76}$$

Where:

$\rho$ = density

Sanchez and Lacombe used the Flory-Huggins expression for the combinatorial entropy of a binary mixture on an incompressible lattice, replacing one component with holes. For the energy, they only considered segment-segment interactions (in other words, segment-hole and hole-hole pair interactions were set equal to zero), and assumed that the segments and the holes are randomly distributed in the lattice. They developed an expression for the Gibbs free energy of a chain fluid on a lattice. By minimizing the Gibbs free energy expression, Sanchez and Lacombe derived the SL EOS:

*Sanchez-Lacombe EOS*

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T}\left[\ln\left(1-\tilde{\rho}\right) + \left(1-\frac{1}{r}\right)\tilde{\rho}\right] = 0 \tag{3.77}$$

Where the reduced quantities are defined by:

$$\tilde{T} = \frac{T}{T^*} \qquad \tilde{P} = \frac{P}{P^*} \qquad \tilde{\rho} = \frac{\rho}{\rho^*} \tag{3.78}$$

The scale factors, $T^*$, $P^*$ and $\rho^*$ are related to lattice variables by:

*Sanchez-Lacombe Parameters*

$$T^* = \frac{\varepsilon^*}{k} \qquad P^* = \frac{\varepsilon^*}{v^*} \qquad \rho^* = \frac{M}{rv^*} \tag{3.79}$$

In the above expressions:

$r$ = number of segments per chain

$\varepsilon^*$ = characteristic interaction energy per segment

$v^*$ = closed-packed volume of a segment

$M$ = molecular weight (for polymer components this is the number average molecular weight)

$k$ = Boltzmann's constant

A pure fluid is characterized completely by three molecular parameters: $\varepsilon^*$, $v^*$, and $r$, or equivalently, the scale factors $T^*$, $P^*$, and $\rho^*$. These parameters are obtained by fitting pure component experimental data, usually data along the saturation curve. Some additional characteristics of the SL EOS are:

- The SL EOS has an explicit size or shape dependency through the molecular parameter $r$. Thus, it takes into account the chain-like structure of long-chain molecules, such as heavy paraffins and polymers.
- SL is more accurate than most cubic equations of state of the van der Waals type (Redlich-Kwong, Peng-Robinson, Redlich-Kwong-Soave, etc.) in calculating liquid volumes.
- SL is not accurate at the critical point of pure fluids; the vapor-liquid equilibrium coexistence curve predicted by the SL EOS is too sharp near critical conditions. Therefore, when experimental vapor pressure data are being regressed, temperatures closer than 15-20°C of the critical point should be omitted.
- Unlike most cubic EOS, the SL EOS does not satisfy a corresponding states principle, except for large molecules $(r \to \infty)$. This is related directly to the fact that the repulsive part of the EOS scales with molecular size through the parameter $r$.
- For polymer molecules, $r$ is very large $(r \to \infty)$. This means that polymeric liquids of high molecular weight satisfy a corresponding states principle.

## Fluid Mixtures

The SL EOS for multicomponent fluid mixtures is identical to the pure-component equation. The difference is that the parameters become composition dependent through mixing rules. These mixing rules are written in terms of volume fractions, rather than mole fractions:

*Sanchez-Lacombe Mixing Rules*

$$\varepsilon^*_{mix} = \frac{1}{v^*_{mix}} \sum_i \sum_j \phi_i \phi_j \varepsilon^*_{ij} v^*_{ij} \quad \textbf{(3.80)}$$

$$v^*_{mix} = \sum_i \sum_j \phi_i \phi_j v^*_{ij} \quad \textbf{(3.81)}$$

$$\frac{1}{r_{mix}} = \sum_j \frac{\phi_j}{r_j} \quad \textbf{(3.82)}$$

Where:

$\phi_i$ = volume fraction of component *i*, defined by:

$$\phi_i = \frac{\frac{m_i}{\rho^*_i v^*_i}}{\sum_j \left( \frac{m_j}{\rho^*_j v^*_j} \right)} \quad \textbf{(3.83)}$$

Where:

$m_i$ = weight fraction

The cross parameters are calculated by:

$$v^*_{ij} = \frac{1}{2}\left[ v^*_{ii} + v^*_{jj} \right]\left(1 - \eta_{ij}\right) \quad \textbf{(3.84)}$$

$$\varepsilon^*_{ij} = \sqrt{\varepsilon^*_{ii} \varepsilon^*_{jj}}\left(1 - k_{ij}\right) \quad \textbf{(3.85)}$$

In the above two expressions, $k_{ij}$ and $\eta_{ij}$ are binary interaction parameters that are fitted to experimental VLE and LLE data. Both parameters are symmetric. If no data are available, they are set equal to zero.

The SL EOS is able to predict the thermodynamic properties of multicomponent mixtures through pure-component and binary interaction parameters only.

## Polymer Systems

The same expressions are used for polymer solutions. Since vapor pressure data are unavailable for polymer liquids, the molecular parameters are determined by fitting experimental liquid volume data. In the case of random copolymers, the pure-component parameters depend on the relative composition of the segments or repeat units that form the copolymer. The mixing rules for the characteristic parameters of the copolymer are:

$$v^*_{co} = \sum_{A}^{Nsegt} \sum_{B}^{Nsegt} \phi_A \phi_B v^*_{AB} \qquad \textbf{(3.86)}$$

With:

$\phi_A$ and $\phi_B$ = volume fractions of the segments that form the copolymer (calculated using an equation similar to Equation 3.82)

*Nsegt* = number of distinct segment types present in the polymer chain, and

$$v^*_{AB} = \frac{1}{2}\left[v^*_{AA} + v^*_{BB}\right]\left(1 - 1_{AB}\right) \qquad \textbf{(3.87)}$$

Where:

$v^*_{AA}$ and $v^*_{BB}$ = characteristic volume parameters of the segments *A* and *B*

$1_{AB}$ is used to account for differences in molecular size.

Similarly, for the energy parameter of the copolymer:

$$\varepsilon^*_{co} = \frac{1}{v^*_{co}} \sum_{A}^{Nsegt} \sum_{B}^{Nsegt} \phi_A \phi_B \varepsilon^*_{AB} v^*_{AB} \qquad \textbf{(3.88)}$$

With:

$$\varepsilon^*_{AB} = \sqrt{\varepsilon^*_{AA} \varepsilon^*_{BB}}\left(1 - m_{AB}\right) \qquad \textbf{(3.89)}$$

Where:

$\varepsilon^*_{AA}$ and $\varepsilon^*_{BB}$ = characteristic energy parameters for the segments *A* and *B*

$m_{AB}$ = correction to the geometric-mean rule

Finally, for the molecular size of the copolymer:

$$\frac{1}{r_{co}} = \sum_{B}^{Nsegt} \frac{\phi_B}{r_B} \qquad \textbf{(3.90)}$$

Where:

$r_B$ = characteristic size parameters of segments *A* and *B*

The characteristic parameters $\varepsilon^*$, $v^*$, and *r* for the segments *A* and *B* are obtained from data on the homopolymers *A* and *B*, respectively.

McHugh and coworkers (Hasch et al, 1992) have shown that the correction terms $1_{AB}$ and $m_{AB}$ have little effect on calculated copolymer phase behavior. For this reason, these two binary parameters are not used in the model and have not been made available for user input. The SL EOS is able to predict UCST and LCST types of phase immiscibility..

If parameters $T^*$, $P^*$, and $\rho^*$ are provided for the polymer or oligomer, then these have highest priority and are used for calculations. If they are not known, usually in the case of copolymers, the user must provide these parameters for the segments that compose the copolymer.

## Sanchez-Lacombe Model Parameters

The Sanchez- Lacombe model parameters are listed in Table 3.22. Appendix B lists parameters for several polymers and monomers. These parameters may be fitted from experimental data if they are not readily available.

***Table 3.22 Sanchez-Lacombe Model Parameters***

| Parameter Name / Element | Symbol | Default | Lower Limit | Upper Limit | Units Keyword | Comments |
|---|---|---|---|---|---|---|
| SLTSTR | $T^*$ | --- | --- | --- | TEMPERATURE | Unary |
| SLPSTR | $P^*$ | --- | --- | --- | PRESSURE | Unary |
| SLRSTR | $\rho^*$ | --- | --- | --- | DENSITY | Unary |
| SLKIJ | $k_{ij}$ | 0.0 | --- | --- | --- | Binary, Symmetric |
| SLETIJ | $\eta_{ij}$ | 0.0 | --- | --- | --- | Binary, Symmetric |

# SPECIFYING THE SANCHEZ-LACOMBE EOS MODEL

See Specifying Physical Properties in Section 3.1.

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# 3.10 POLYMER SRK EOS MODEL

This section describes the Soave-Redlich-Kwong (SRK) cubic equation of state (EOS) extended to mixtures containing polymers. This model will be referred to as the polymer SRK EOS. From modeling point of view, this model is considered similar to the PSRK EOS model available in Aspen Plus for conventional mixtures. Like the PSRK model, for mixture applications this model uses a Huron-Vidal-type mixing rule that incorporates an excess energy (Gibbs or Helmholtz) term. The detailed discussion of these types of mixing rules can be found elsewhere (see *Aspen Plus Physical Property Methods and Models,* also see Orbey and Sandler, 1995, 1997; Fischer and Gmehling, 1996). Here the basic characteristics of the model are summarized from a modeling perspective.

Topics covered include:

- Summary of Applicability
- Polymer SRK EOS Model
- Specifying the Polymer SRK EOS Model

# SUMMARY OF APPLICABILITY

Depending upon the nature of an application, either an activity coefficient model or an EOS is preferable. Some general points concerning the model selection are as follows:

1. Most activity coefficient models do not account for the pressure (or compressibility) effects, and therefore they are only applicable to incompressible fluids. On the other hand, some of the phase behavior consistently observed in polymer mixtures depend, at least partly, on the compressibility of mixture. The most important of them is the so-called lower critical solution temperature (LCST). Equations of state take the compressibility into account, and thus they are more suitable for modeling of the polymer-mixture phase behavior at higher pressures where the compressibility of the mixture becomes significant, and an LCST is expected.
2. In contrast to the activity coefficient models, the EOS models are suitable for calculation of both phase equilibrium and other thermophysical properties such as enthalpy, entropy, Gibbs energy simultaneously from the same model. Moreover, they are applicable to both vapor and liquid phases at the same time (the activity coefficient models are only applicable to the liquid phase, and for the vapor phase another model is needed).
3. Equations of state are developed first as pure-component models and subsequently extended to mixtures. Thus, it is possible to use these models to provide information for both pure components and mixtures simultaneously.

The polymer SRK EOS and the Sanchez-Lacombe EOS can be used alternatively under similar circumstances. The first one is an extension of an EOS primarily developed for conventional components to polymers, whilst the latter is an EOS developed primarily for polymer molecules and extended to conventional components. It is not easy to establish criteria for selection of a particular model over the other, and the user may need to test alternatives against available experimental information. A third EOS option is the polymer SAFT model (See Section 3.11), which can be considered as a model that combines the benefits of the polymer SRK and polymer Sanchez-Lacombe equations.

# POLYMER SRK EOS MODEL

The excess Gibbs free energy can be written from an EOS using rigorous thermodynamics, and it can be equated to the same property from an activity coefficient model:

$$\frac{G^E_{EOS}}{RT} = \ln\phi - \sum x_i \ln\phi_i^* \equiv \sum x_i \ln\gamma_i = \frac{G^E_\gamma}{RT} \qquad \textbf{(3.91)}$$

Above $\phi_i$ and $\phi_i^*$ are the overall mixture fugacity and fugacity of component *i* in that mixture respectively, $G^E$ is the molar excess Gibbs free energy, *R* is gas constant and *T* is absolute temperature. The subscripts *EOS* and $\gamma$ represent properties obtained from an EOS model and from an activity coefficient model respectively. The above equality can only be written at a selected reference pressure. A reference for pressure is needed since the Gibbs free energy from an EOS is pressure dependent but the same term from an activity coefficient is not. Thus, an algebraically explicit equality can only be established at a single reference pressure.

The usual alternatives for the reference pressure are either P=0 or P=∞. There is much debate as to which selection is better (Orbey and Sandler, 1995, 1997; Fischer and Gmehling, 1996), and it is beyond the scope of this manual. In general, the combination of an EOS with an activity coefficient model by equating the Gibbs free energy terms leads to a general functional relation between the *a* and *b* parameters of an EOS in the form:

$$\frac{a}{bRT} = \Gamma\left(a_i, b_i, x_i, G^E_\gamma \text{ or } A^E_\gamma\right) \qquad \textbf{(3.92)}$$

Above the subscript *i* indicates pure component property, *x* is mole fraction, and *A* is Helmholtz free energy. The functional form $\Gamma$ depends on the selection of reference pressure. Holderbaum and Gmehling (1991) used this approach for the SRK EOS to develop the following relation at the limit of low (atmospheric) pressure:

*Soave-Redlich-Kwong EOS*

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)} \qquad \textbf{(3.93)}$$

$$\frac{a}{bRT} = \sum_i x_i \frac{a_i}{RTb_i} - 1.546\left(\frac{G^E_\gamma}{RT} + \sum_i x_i \ln\frac{b}{b_i}\right) \qquad \textbf{(3.94)}$$

For the co-volume parameter, *b*, the linear mixing rule $b = \sum x_i b_i$ was used. With Equation 3.94, this completely defines the *a* and *b* parameters of the SRK EOS for any mixture, provided that an activity coefficient model is selected to represent the molar excess Gibbs energy term $G_\gamma^E$. In the original PSRK EOS, the UNIFAC predictive model was used for this purpose. For the polymer SRK model here, the POLYNRTL model proposed for polymer mixtures is used (see Section 3.5 for the details of the POLYNRTL model). Consequently, the same mixture interaction parameters used in the POLYNRTL model are used in the polymer SRK model, only this time in the EOS format.

In modeling polymer containing mixtures with the polymer SRK EOS, one needs values of the critical temperature, the critical pressure, and component-specific constants of Mathias and Copeman (1989) for each constituent of the mixture to evaluate pure component $a_i$ and $b_i$'s. (See *Aspen Plus Physical Property Methods and Models* for more details on the Mathias-Copeman constants for the SRK EOS).

For conventional components, values of the pure component constants are readily available and stored in the Aspen Plus databanks. For oligomers and polymers, these parameters are not available. To overcome this drawback, some estimation techniques have been suggested by several researchers based on the available experimental values for $T_c$ and $P_c$ for alkanes up to about $C_{20}$ (See works of Tsonopoulos and Tan, 1993; Teja et al., 1990). The user needs to supply these constants for the polymers and oligomers using the guidelines given in the *Model Parameters for the Polymer SRK EOS* section below.

Most two-parameter cubic equations of state (RKS, Peng-Robinson, so on and so forth) can not predict the molar volumes in the liquid phase accurately. To overcome this difficulty, the Rackett model is used to overwrite the liquid molar volume predictions of the EOS in PSRK property method in Aspen Plus. In the case of the polymer SRK EOS, the Van Krevelen model (See Section 3.1) is used for the polymer and oligomer components; the Rackett equation still is used for conventional components. Mixture liquid molar volumes are calculated using the ideal-mixing assumption.

## Polymer SRK EOS Model Parameters

To use the polymer SRK EOS, the pure components parameters needed are the critical constants $T_c$, $P_c$ and the Mathias-Copeman constants. Table 3.23 shows these unary parameters. For the conventional components, they are available from the Aspen Plus data bank. For oligomers and polymers, user needs to provide them using unary parameter forms.

***Table 3.23 Unary Parameters for the Polymer SRK EOS***

| Parameter Name / Element | Symbol | Default | Lower Limit | Upper Limit | SI Units | Comments |
|---|---|---|---|---|---|---|
| TCRKS | $T_{c,i}$ | TC | 5 | 5000 | K | Unary |
| PCRKS | $P_{ci}$ | PC | $10^5$ | $10^8$ | $N/m^2$ | Unary |
| RKSMCP/1 | $c_{1,i}$ | 0 | --- | --- | --- | Unary |
| RKSMCP/2 | $c_{2,i}$ | --- | --- | --- | --- | Unary |
| RKSMCP/3 | $c_{3,i}$ | --- | --- | --- | --- | Unary |

*Critical Constants for Polymers*

Polymers are not supposed to vaporize, and therefore for the critical temperature of the polymers a high value is recommended (typically $T_c > 1000K$). For the same reason, a relatively low critical pressure is needed ($P_c < 10^6 N/m^2$). For all of the Mathias-Copeman parameters for oligomers and polymers, zero is recommended due to unavailability of information on polymer vapor pressure, though the user may overwrite them. For oligomers, critical temperatures lower than those used for polymers and critical pressures higher than that of polymers can be used. Depending upon the magnitude of these choices, some oligomer may appear in the vapor phase. For the selection of these constants for oligomers, the works of Tsonopoulos and Tan (1993) and Teja et al. (1990) can be used as a guideline. The $T_c$ and $P_c$ profiles obtained by Tsonopoulos and by Teja for alkane hydrocarbons are shown in Figure 3.9. In some cases, the choices for the critical constants for polymers and oligomers may affect the VLE calculations significantly. This largely depends on the nature of the solvents present and the temperature and pressure at which the phase calculations are made. None of the parameters in Table 3.23 are automatically supplied by Polymers Plus for oligomers and polymers. The user needs to enter them using unary parameter forms.

The default option for the excess energy model used in the polymer SRK model is the polymer NRTL activity coefficient model. Therefore, the same binary interaction parameters needed for the polymer NRTL model will also be required in this application. The polymer NRTL model is described in Section 3.5. The user may overwrite this choice by creating her/his own property method selecting another activity coefficient model for the evaluation of $G_{\gamma}^{E}$ term in the polymer SRK model. In such a case the mixture parameters of the selected $G_{\gamma}^{E}$ model are to be supplied.

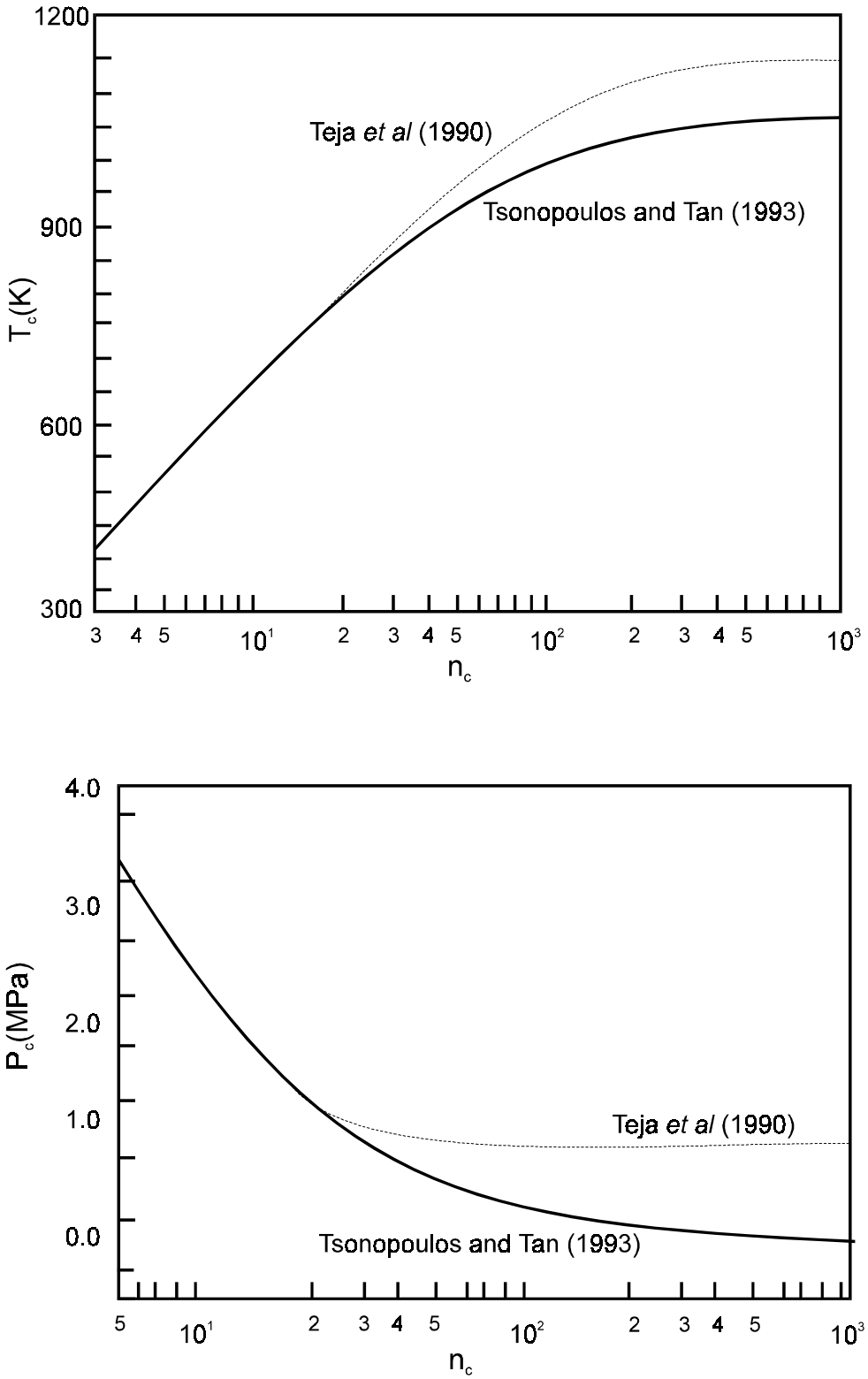


***Figure 3.9*** *Critical Temperature and Pressure Versus Carbon Number*

# SPECIFYING THE POLYMER SRK EOS MODEL

See Specifying Physical Properties in Section 3.1.

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# 3.11 SAFT EQUATION-OF-STATE MODEL

This section describes the statistical associating fluid theory (SAFT). This equation of state will be used through the POLYSAFT property method. SAFT is a rigorous thermodynamic model based on the perturbation theory of fluids. The equation of state accounts explicitly for the molecular repulsions, the chain connectivity, dispersion (attractive) forces, and specific interactions via hydrogen bonding.

Topics covered include:

- Summary of Applicability
- SAFT EOS Model
- Application of SAFT
- Specifying the SAFT EOS Model

## SUMMARY OF APPLICABILITY

The Statistical Associating Fluid Theory was developed by Gubbins and co-workers (Chapman et al., 1990), and was first used for engineering calculations by Huang and Radosz (Huang and Radosz, 1990; 1991).

The SAFT EOS currently represents a state-of-the-art engineering tool for the thermodynamic properties and phase equilibria correlation and prediction of polymer-containing systems. It has a sound theoretical foundation, based on the perturbation theory of fluids, and has terms that account explicitly for the effects of molecular size (covalent bonding), attractive interactions, and specific interactions (hydrogen bonding). This way the SAFT model is applicable to a wide variety of systems, over a wide variety of conditions.

Recent research efforts by various research groups worldwide have demonstrated the applicability of SAFT to a variety of polymer systems. These include low-density polyethylene (Folie and Radosz, 1995; Xiong and Kiran, 1995), polystyrene (Pradham et al., 1994), poly(ethylene-propylene) copolymer (Chen et al., 1992), polyisobutylene (Gregg et al., 1994), poly(ethylene-methyl acrylate) copolymers (Lee et al., 1996), poly(ethylene-acrylic acid) copolymers (Lee et al., 1994; Hasch and McHugh, 1995), and many others. The above researchers, together with others in the field of polymer thermodynamics, have found that the SAFT equation of state is able to correlate accurately the thermodynamic properties and phase behavior of both pure-components and their mixtures. In addition, SAFT has shown remarkable predictive capability, which is a very important feature for modeling industrial applications.

# SAFT EOS MODEL

The statistical associating fluid theory is a molecularly-based equation of state, which means that it evaluates the properties of fluids based on interactions at the molecular level. This way the model is able to separate and quantify the effects of molecular structure and interactions on bulk properties and phase behavior. Examples of such effects are:

- Molecular size and shape (e.g., chain length)
- Association energy (e.g., hydrogen bonding)
- Attractive (e.g., dispersion) energy

In developing any equation of state based on theoretical considerations, a *model fluid* has to be selected. In the case of SAFT, Chapman et al. chose a model fluid that is a mixture of equal-sized spherical segments interacting with square-well potential (Chapman et al., 1990). To make the model fluid more realistic, two kinds of bonds where also considered between the segments: covalent-like bonds, that form chain molecules, and hydrogen bonds. As a result, the model fluid can represent a wide variety of real fluids such as:

- Small nearly-spherical species (methane, ethane, etc.)
- Chain molecules (alkanes, polymers)
- Associating species (alkanols)

The reduced density $\eta$ of the fluid (segment packing fraction) is defined as:

$$\eta = \frac{\pi N_{AV}}{6} \rho m d^3 \qquad \textbf{(3.95)}$$

Where:

$\rho$ = molar density

$m$ = number of segments in each molecule

$d$ = effective segment diameter (temperature dependent)

Equation 3.95 can be rewritten as:

$$\eta = \tau\rho m v^o \quad \textbf{(3.96)}$$

Where:

$\tau$ = constant equal to 0.74048

$v^0$ = *segmental molar volume at closed-packing* (the volume occupied by a mole of closely packed segments), in units of cc per mole of segments

From Equations 3.95 and 3.96 it falls that $v^0$ is temperature dependent, since it depends on the temperature dependent diameter *d*. Thus, it is convenient to define a *temperature-independent segmental molar volume* at $T$=0, denoted $v^{oo}$. This parameter will be referred to as the *segment volume*. Chen and Kreglewski solved the Barker-Henderson integral equation of the diameter *d* (which depends on the square-well potential), and proposed the following expression between $v^o$ and $v^{oo}$ (Chen and Kreglewski, 1977):

$$v^o = v^{oo}\left[1 - C\exp\left(\frac{-3u^o}{kT}\right)\right]^{33} \quad \textbf{(3.97)}$$

In the above equation, $u^o / k$ is the square-well depth, a temperature-independent energy parameter, referred to as the *segment energy*, in Kelvins. Chen and Kreglewski set the constant $C$=0.12, and used the following temperature dependence of the dispersion energy of interaction between segments( Chen and Kreglewski, 1977):

$$u = u^o\left[1 + \frac{e}{kT}\right] \quad \textbf{(3.98)}$$

Where:

$e/k$ = constant (whose values will be provided later)

SAFT was proposed by Gubbins, Radosz, and co-workers (Chapman et al., 1990). The main idea in SAFT is perturbation theory. In perturbation theory, the fluid is simulated using a *reference* fluid. The reference fluid is usually a well-understood and well-described fluid (such as the hard-sphere fluid). Any deviations between the properties of the real and the reference fluid are referred to as *perturbations*. Chapman et al. used a reference fluid that incorporates both the chain length (molecular size and shape) and the molecular association (whenever applicable). (In most pre-existing engineering equations of state, the much simpler hard-sphere fluid had been used as the reference fluid).

To derive the equation of state for the reference fluid, Chapman et al. needed expressions for the *Helmholtz free energy* for the chain and association effects (Chapman et al., 1990). These researchers used Wertheim's expressions for chain and hydrogen bonding, which are based on cluster expansion theory (Wertheim, 1984; 1986a,b) . (As a reminder, equation of state developers often derive expressions for the Helmholtz free energy for convenience reasons: most properties of interest, such as the system pressure, can be easily obtained via simple algebraic differentiation of the Helmholtz free energy.)

As mentioned above, the reference equation of state in SAFT accounts for the hard-sphere, chain, and association effects. The effects of other kinds of intermolecular forces, such as dispersion forces, are usually weaker, and are treated through a perturbation term. Chapman et al. (1990) used an expression similar to that of Alder et al. for the square-well potential (Alder et al, 1972).

The statistical associating fluid theory results in an expression of the residual Helmholtz free energy, $a^{res}$ per mole, defined as:

$$a^{res}(T,V,N) = a(T,V,N) - a^{ideal}(T,V,N) \quad \textbf{(3.99)}$$

Where:

a(T,V,N) = total Helmholtz energy per mole at the same temperature and volume as:

$a^{ideal}$ (T,V,N) = ideal-gas Helmholtz energy per mole

In SAFT, the residual Helmholtz free energy $a^{res}$ is a sum of three contributions:

- $a^{seg}$ represents segment-segment interactions (hard-sphere repulsions and attractive or dispersion forces)
- $a^{chain}$ is due to the presence of covalent chain-forming bonds among the segments
- $a^{assoc}$ is present when the fluid exhibits hydrogen bonding interactions among the segments

The general expression for the Helmholtz free energy in SAFT is given by:

$$a^{res} = a^{seg} + a^{chain} + a^{assoc} \quad \textbf{(3.100)}$$

The segment contribution $a^{seg}$ per mole of molecules is given by:

$$a^{seg} = m\left(a_0^{hs} + a_0^{disp}\right) \quad \textbf{(3.101)}$$

Where *m* is the number of segments on the chain, and the two contributions represent the *segmental* hard-sphere and dispersion interactions. These two quantities are given by:

*Hard-Sphere Term*

$$\frac{a_0^{hs}}{RT} = \frac{4\eta - 3\eta^2}{(1-\eta)^2} \quad \textbf{(3.102)}$$

*Dispersion Term*

$$\frac{a_0^{disp}}{RT} = \sum_i \sum_j D_{ij} \left[\frac{u}{kT}\right]^i \left[\frac{\eta}{\tau}\right]^j \quad \textbf{(3.103)}$$

Equation 3.102 is the well-known Carnahan-Starling expression for the hard-sphere fluid ($\eta$ is the reduced density, given by Equations 3.95 and 3.96) (Carnahan and Starling, 1972) . The dispersion term, given by Equation 3.103, is a fourth-order perturbation expansion of the Helmholtz free energy, initially fitted by Alder et al. to molecular dynamics simulation data for the square-well fluid (Alder et al., 1972). This equation also provided the basis for the perturbed hard-sphere theory (PHCT) of Donohue and Prausnitz (Donohue and Prausnitz, 1976). In Equation 3.103, $D_{ij}$ are universal constants. In SAFT, Huang and Radosz used the $D_{ij}$ constants that were proposed by Chen and Kreglewski, who re-fitted Alder's expression to very accurate experimental data for argon (Huang and Radosz, 1990; Chen and Kreglewski, 1977) . The dispersion energy of interaction per segment, *u*, is given by Equation 3.98.

The chain and association terms in SAFT are the result of Wertheim's thermodynamic theory of polymerization. This section does not deal with associating species, and therefore, the association term will be neglected. The chain term, which represents the Helmholtz free energy increment due to the formation of covalent bonds, is given by the following expression (Chapman et al., 1990):

*Chain Term*

$$\frac{a^{chain}}{RT} = (1-m)\ln g(d)^{seg} \qquad \textbf{(3.104)}$$

Where $g(d)^{seg}$ is the value of the segmental radial distribution function at a distance equal to the effective segment diameter *d*. In other words, $g(d)^{seg}$ is the radial distribution function at the surface of the segment, or the *contact value*. As explained by Chapman et al. and Huang and Radosz, Equation 3.104 is derived from the association theory by replacing the hydrogen bonds with covalent, chain-forming bonds (Chapman et al., 1990; Huang and Radosz, 1990). As mentioned above, in SAFT the segments are approximated by hard spheres, and thus, $g(d)^{seg}$ can be approximated by the hard-sphere radial distribution function (Carnahan and Starling, 1972):

$$g(d)^{seg} \approx g(d)^{hs} = \frac{1-\frac{1}{2}\eta}{(1-\eta)^3} \qquad \textbf{(3.105)}$$

Therefore, the chain contribution to the free energy in SAFT (Equation 3.104) can be rewritten as:

$$\frac{a^{chain}}{RT} = (1-m)\ln\frac{1-\frac{1}{2}\eta}{(1-\eta)^3} \qquad \textbf{(3.106)}$$

*Compressibility Factor*

The compressibility factor $Z$ can be easily obtained by taking the molar volume derivative of the residual Helmholtz free energy; the resulting SAFT equation of state has the form:

$$Z = \frac{Pv}{RT} = 1 + Z^{seg} + Z^{chain} + Z^{assoc} \quad \textbf{(3.107)}$$

Where:

$$Z^{seg} = m\left[\frac{4\eta - 2\eta^2}{(1-\eta)^3} + \sum_i \sum_j jD_{ij}\left[\frac{u}{kT}\right]^i \left[\frac{\eta}{\tau}\right]^j\right] \quad \textbf{(3.108)}$$

$$Z^{chain} = (1-m)\frac{\frac{5}{2}\eta - \eta^2}{(1-\eta)\left(1-\frac{1}{2}\eta\right)} \quad \textbf{(3.109)}$$

The contribution from association, $Z^{assoc}$ is not considered for the time being, and thus this term will be zero.

The SAFT equation of state presented above has been used to correlate vapor pressures and liquid densities of over 100 real fluids by Huang and Radosz (Huang and Radosz, 1990). For each fluid, three parameters were fitted to the experimental data:

- Segment volume $v^{oo}$
- Segment energy $u^o / k$
- Segment number $m$

Estimated parameters for these fluids are given in Appendix F.

## Extension to Fluid Mixtures

The SAFT equation of state was extended to treat multicomponent fluid mixtures by Huang and Radosz (Huang and Radosz, 1991). In doing so, they took advantage of the fact that SAFT was based on theoretical arguments and therefore, the extension of the equation of state from pure components to mixtures is straightforward, based on statistical mechanical considerations.

For the extension of the hard-sphere term to mixtures, Huang and Radosz (Huang and Radosz, 1991) used the theoretical result of Mansoori et al. for the Helmholtz free energy of a mixture of hard spheres, which is given by the following expression (Mansoori et al., 1971):

$$\frac{a^{hs}}{RT} = \frac{6}{\pi\rho}\left[\frac{(\zeta_2)^3 + 3\zeta_1\zeta_2\zeta_3 - 3\zeta_1\zeta_2(\zeta_3)^2}{\zeta_3(1-\zeta_3)^2} - \left[\zeta_0 - \frac{(\zeta_2)^3}{(\zeta_3)^2}\right]\ln(1-\zeta_3)\right] \quad \textbf{(3.110)}$$

Where:

$\zeta_k$ = functions of the density ρ, given by Chapman et al. (Chapman et al., 1990):

$$\zeta_k = \frac{\pi N_{Av}}{6}\rho\sum_i x_i m_i \left(d_{ii}\right)^k \quad \textbf{(3.111)}$$

Where:

$x_i$ = mole fraction of the *i*-th component

Note that Equation 3.110 reduces to the same result for pure components, as given by Equation 3.101 and Equation 3.102, in the limit of $x_i$ of unity.

In a similar fashion, the chain contribution for fluid mixtures is a direct extension of the pure-component result:

$$\frac{a^{chain}}{RT} = \sum_i x_i \left(1 - m_i\right) \ln\left(g_{ii}\left(d_{ii}\right)^{hs}\right) \quad \textbf{(3.112)}$$

Where $g_{ii}$ is the radial distribution function of two species *i* in a mixture of spheres, evaluated at the hard-sphere contact. This value was derived from statistical mechanics by Mansoori et al., and has the form (Mansoori, 1971):

$$g_{ii}\left(d_{ii}\right)^{seg} \approx g_{ii}\left(d_{ii}\right)^{hs} = \frac{1}{1-\zeta_3} + \frac{3d_{ii}}{2}\frac{\zeta_2}{\left(1-\zeta_3\right)^2} + 2\left[\frac{d_{ii}}{2}\right]^2 \frac{\zeta_2^2}{\left(1-\zeta_3\right)^3} \quad \textbf{(3.113)}$$

For the dispersion (attractive) term in SAFT, Huang and Radosz used several approaches for its extension to fluid mixtures (Huang and Radosz, 1991). One of these approaches, the *conformal solution* approach (which has been considered by most researchers who have applied SAFT to engineering calculations) is discussed here. According to the conformal solution, or van der Waals one-fluid (vdW1), theory, a fluid mixture is approximated by a hypothetical *pure* fluid having the same molecular energy and size (volume). The vdW1 theory leads to the vdW1 mixing rules. For the energy parameter in SAFT, the vdW1 mixing rule is:

*Dispersion Energy Mixing Rule*

$$\frac{u}{kT} = \frac{\sum_i \sum_j x_i x_j m_i m_j \frac{u_{ij}}{kT}\left(v^o\right)_{ij}}{\sum_i \sum_j x_i x_j m_i m_j \left(v^o\right)_{ij}} \quad \textbf{(3.114)}$$

Where:

$$\left(v^o\right)_{ij} = \left[\frac{\left(v^o\right)_i^{1/3} + \left(v^o\right)_j^{1/3}}{2}\right]^3 \quad \textbf{(3.115)}$$

$$u_{ij} = \sqrt{u_{ii}u_{jj}}\left(1 - k_{ij}\right) \quad \textbf{(3.116)}$$

Where $k_{ij}$ is an empirical binary parameter, fitted to experimental VLE or LLE data.

In SAFT, the molecular size is taken into account via the segment number *m*. Therefore, Huang and Radosz applied the vdW1 mixing rule for the parameter *m* (Huang and Radosz, 1991):

$$m = \sum_i \sum_j x_i x_j m_{ij} \quad \textbf{(3.117)}$$

Where:

$$m_{ij} = \frac{m_i + m_j}{2}\left(1 - l_{ij}\right) \quad \textbf{(3.118)}$$

In the above equation, $l_{ij}$ is another empirical binary parameter, fitted to experimental data. In the absence of mixture data, both binary parameters $k_{ij}$ and $l_{ij}$ are equal to zero.

# APPLICATION OF SAFT

Huang and Radosz have proposed a comprehensive parametrization of the SAFT equation of state based on the work by Topliss, that facilitates the coding of the SAFT individual terms and their derivatives with respect to density and composition (Huang and Radosz, 1991; Topliss, 1985). This approach has been followed in Polymers Plus. All individual terms and their derivatives are provided in the Huang and Radosz paper, and will not be reproduced here (Huang and Radosz, 1991).

To apply SAFT to real fluid systems, three pure-component (unary) parameters need to be provided for each species: the *segment volume* $v^{oo}$, the *segment energy* $u^o / k$, and the *segment number m.* These parameters are estimated by fitting vapor-pressure and liquid-density experimental data for the pure components. Huang and Radosz have evaluated pure-component parameters for about 100 species; these parameters are also tabulated in Appendix F for convenience (Huang and Radosz, 1990). In case the component of interest is not included in the list of components with already available parameters, the user needs to set up a regression run (DRS), and use vapor-pressure and liquid density experimental data to estimate the necessary parameters $v^o$, $u^o / k$, and *m*.

For the components that Huang and Radosz regressed experimental data and obtained parameters, they reported percent average absolute deviations in vapor pressures and liquid densities (Huang and Radosz, 1991). The quality of their fit is very good, as can be usually expected for a reasonable, three parameter equation of state. However, the advantage of SAFT is the behavior of its parameters. This means that the SAFT unary parameters follow expected trends, which makes their estimation possible in the absence of experimental data. This is very important because engineers are often dealing with polydispersed, poorly defined pseudocomponents of real fluid mixtures, whose parameters can not be fitted due to the absence of experimental information. The fact that the parameter values are well-behaved and suggest predictable trends upon increasing the molar mass of components in the same homologous series gives SAFT a predictive capability in the absence of experimental data.

*SAFT Parameter Generalization*

To understand this important concept better, it helps to remember what the three SAFT parameters represent. The segment energy $u^o / k$ and the segment volume $v^{oo}$ are *segmental parameters*, which suggests that they should remain fairly constant between components in the same homologous series. The third parameter *m* represents the number of segments on the chain; this implies that *m* should be proportional to the molecular mass. In the case of normal alkanes, Huang and Radosz proposed the following generalized correlations for the pure-component parameters:

$$m = 0.70402 + 0.046647\,MW \qquad \textbf{(3.119)}$$

$$mv^{oo} = 11.888 + 0.55187\,MW \qquad \textbf{(3.120)}$$

$$\frac{u^o}{k} = 210.0 - 26.886\exp[-0.013341\,MW] \qquad \textbf{(3.121)}$$

In the above three expressions, *MW* is the component molecular weight (for polymer components, it is the number average molecular weight). The units of $v^{oo}$ are $cm^3 / mole$, and the units of $u^o / k$ are in Kelvin. Equation 3.120 and Equation 3.121 suggest that as the *MW* becomes a very large number (polymer components), $v^{oo}$ and $u^o / k$ will assume some limiting values. Huang and Radosz also have proposed generalized correlations for other kinds of organic compounds, such as polynuclear aromatics, n-alkylbenzenes, and others (Huang and Radosz, 1991). These can be found in the original reference, and will not be reproduced here.

As mentioned earlier, the temperature dependence of the energy *u* in SAFT is given by Equation 3.98. In that equation, the parameter *e/k* is a constant that was related to the acentric factor and the critical temperature by Chen and Krewlewski (Chen and Krewlewski, 1977). Since in SAFT the energy parameter is between segments rather than components, Huang and Radosz set *e/k*=10 for all components. They only proposed a few exceptions for some small molecules: *e/k*=0 for argon; 1 for methane, ammonia, and water; 3 for nitrogen; 4.2 for carbon monoxide; 18 for chlorine; 38 for $CS_2$; 40 for $CO_2$; and 88 for $SO_2$.

The three unary parameters $v^{oo}$, $u^o / k$, and *m* for each component represent the necessary user input to apply SAFT to real fluid systems (together with the value of *e/k*). For fine tuning of mixture phase behavior, the binary parameters $k_{ij}$ and $l_{ij}$ can be regressed to available phase equilibrium data from the literature and/or the lab. The values of these binary parameters are usually close to zero.

## SAFT EOS Model Parameters

The SAFT model parameters are listed in Table 3.24.

***Table 3.24 Unary parameters for the SAFT EOS***

| Parameter Name / Element | Symbol | Default | Lower Limit | Upper Limit | SI Units | Comments |
|---|---|---|---|---|---|---|
| SAFTM | m | --- | --- | --- | --- | Unary |
| SAFTV | $v^{oo}$ | --- | --- | --- | MOLE-VOLUME | Unary |
| SAFTU | $u^o / k$ | --- | --- | --- | TEMP | Unary |
| SFTEPS | e/k | 10 | --- | --- | --- | Unary |
| SFTKIJ | kij | 0 | --- | --- | --- | Binary |
| SFTLIJ | lij | 0 | --- | --- | --- | Binary |

For each component, SAFTM, SAFTV, and SAFTU unary parameters have to be specified. The parameter SFTEPS has a default value of 10, which applies to most species (see text for some exceptions). Parameters SFTKIJ and SFTLIJ are binary parameters between components of the fluid. They have a default value of zero, and they can be regressed to phase equilibrium data for binaries.

# SPECIFYING THE SAFT EOS MODEL

See Specifying Physical Properties in Section 3.1.

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# 4 POLYMERIZATION REACTIONS

This chapter discusses polymerization mechanisms and kinetics.

Topics discussed in the introductory section include:

- Polymerization Reaction Categories
- Polymerization Process Types
- Polymers Plus Reaction Models

Following an introduction which provides background information of the subject, a separate section is devoted to each of the polymerization kinetic models available in Polymers Plus.


| SECTIONS | | PAGE |
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| 4.1 | Step-Growth Polymerization Model | (4•11) |
| 4.2 | Free-Radical Bulk Polymerization | (4•95) |
| 4.3 | Emulsion Polymerization Model | (4•121) |
| 4.4 | Ziegler-Natta Polymerization Model | (4•151) |
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| 4.6 | Segment-Based Reaction Model | (4•193) |

# POLYMERIZATION REACTION CATEGORIES

Over the years, many classifications have been developed for polymerization reactions. One classification divides them into *condensation* and *addition* polymerization.

*Condensation Polymerization*

Condensation polymerization results in the elimination of a smaller molecule, water for example, through the reaction of bi- or polyfunctional monomers.

*Addition Polymerization*

Addition polymerization, on the other hand, does not produce small molecule byproducts. The repeating units within the polymer have the same structure as the monomers from which they originated.

The problem with this classification is that while it describes differences in the molecular structure of the resulting polymer, it does not fully capture the differences in the reaction mechanism. Furthermore, a given polymer can be made by more then one pathway, one which would result in an addition polymer, and one which would result in a condensation polymer, by this classification.

For example, Nylon-6 can be made through a caprolactam, and therefore be labeled an addition polymer, or through an  -aminohexanoic acid, and in this case be labeled a condensation polymer.

*Step Growth and Chain Growth Polymerization*

A classification which is more useful for capturing the difference in the mechanisms through which polymers are produced divides polymerization reactions into *step-growth* and *chain-growth* polymerization. The differences between step-growth and chain-growth polymerization are summarized in Tables 4.1 and 4.2.

### *Table 4.1 Comparison of Step-Growth to Chain-Growth Polymerization*

| | Step Growth | Chain Growth |
|---|---|---|
| Monomer type | Bi-, polyfunctional | No functionality |
| Reaction categories | Single intermolecular reaction | Several consecutive reactions for initiation, growth, and termination |
| Reacting species | Any combination of monomers, oligomers, polymer chains | Monomers and active centers (free-radical, ion, polymer, catalyst end) |
| Elimination product | Small molecule elimination product for condensation polymerization only | None |
| Polymer growth rate | Slow, chain lifetime of the order of hours | Rapid, chain lifetime of the order of seconds |
| Polymer size | High molecular weight at high conversion | High molecular weight at all conversion levels |

### *Table 4.2 Step-Growth and Chain-Growth Polymerization Reaction Types*

| Reaction Type | Active Center | Initiation | Growth Reaction |
|---|---|---|---|
| **Step Growth** | | | |
| Condensation | Bi-, polyfunctional end groups | None | Nucleophilic substitution |
| Pseudo condensation | Bi-, polyfunctional end groups | None | Nucleophilic addition |
| Ring Scission | Bi-, polyfunctional end groups | Yes for ring opening | Nucleophilic addition or substitution |
| **Chain Growth** | | | |
| Free-radical | Free radical | Chemical, thermal, radiative | Monomers add on to radical |
| Coordination | Metal complex | Catalyst activation | Monomers insert into metal complex carbon bond |
| Ionic | Anion or cation | Dissociation | Monomers add on at ion pair |

# Step-Growth Polymerization

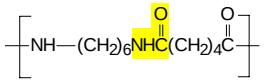
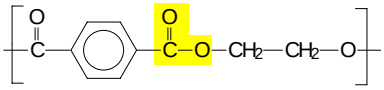
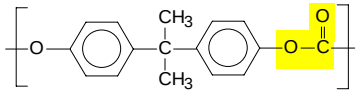
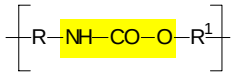
Step-growth polymerization retains the definition given for condensation polymers for the majority of cases, i.e. monomers react with each other to eliminate small molecules. Step-growth polymers are formed through the same reaction type occurring between functional groups located on any combination of monomers, oligomers, or polymer chains. The polymer chains continue to grow from both ends as polymerization progresses. The reactions occur at a relatively slow rate and chains grow slowly.

Some examples of step-growth polymers include polyamides, polyesters, polycarbonates, and polyurethanes (see Chapter 2 for a discussion of polymer types based on molecular structure).

*Step Growth Polymer Categories*

Step-growth polymerization can be sub-categorized as *condensation*, *pseudocondensation*, and *ring-opening* or *ring-scission* depending on the chemical pathways through which the reactions occur. Table 4.3 lists typical step-growth polymers. For each polymer, the main reacting monomers are shown, along with the reaction type.

### *Table 4.3 Typical Commercial Step-Growth Polymers*

| Polymer (Trade Name) | Monomers | Repeat Unit | Reaction Type | Applications (Similar Polymers) |
|---|---|---|---|---|
| Polyamide (Nylon 6,6) | Adipic acid Hexamethylene diamine |  | Dicarboxylic acid + diamines | Fiber, plastics (lycra, Nylon 6) |
| Polyester (PET) | Terephthalic acid Ethylene glycol |  | Dicarboxylic onhydride + glycols | Fiber (PBT, Dacron, Nylon) |
| Polycarbonate (Lexan) | Bisphenol-A Phosgene |  | Dihydroxy reactant + Phosgene | Lenses, packaging (Merlon) |
| Polyurethane | Toluene diisoyamate polyether diol |  | Diisocyanate + dialcohol | Foam, packaging |

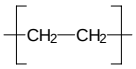
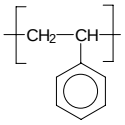
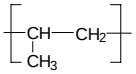
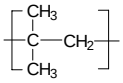
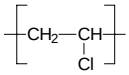
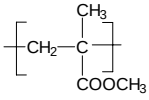
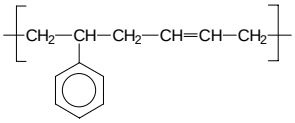
## Chain-Growth Polymerization

Chain growth polymers are formed through the addition of monomers to an active center (free-radical, ion, or polymer-catalyst bond), in a "chain" reaction, at a very fast rate. Furthermore, several different types of reaction occur to initiate, propagate, and terminate polymer growth. Examples of chain growth polymers include various polyolefins, polyvinyls, and several copolymers (styrenic copolymers, for example).

*Chain Growth Polymer Categories*

Chain-growth polymerization can be categorized as *free-radical*, *coordination complex*, or *ionic*, depending on the type and method of formation of the active center. Table 4.4 lists typical commercial chain-growth polymers.

### *Table 4.4 Typical Commercial Chain-Growth Polymers*

| Polymer | Monomers | Repeat Unit | Reaction Types | Applications |
|---|---|---|---|---|
| Polyethylene | Ethylene |  | Bulk/solution (free-radical)<br>Coordination complex (Ziegler-Natta) | Film, packaging |
| Polystyrene | Styrene |  | Bulk/solution/ suspension (free-radical) | Containers, packaging, insulation |
| Polypropylene | Propylene |  | Coordination complex (Ziegler-Natta) | Films, packaging, autoparts, sealants |
| Polyisobutylene | Isobutylene |  | Ionic | Films, plastic tubing |
| Polyvinyl chloride | Vinyl chloride |  | Bulk/solution/ suspension (free-radical) | Floor coverings, pipes |
| Polymethalmethacrylate | Methyl Methacrylate |  | Bulk/solution (free-radical) | Lenses, plastics |
| Styrene butadiene rubber | Styrene Butadiene |  | Emulsion (free-radical) | Tires, belting, shoe soles |

# POLYMERIZATION PROCESS TYPES

*Step Growth Reaction Sub-classes*

In addition to chemical pathways, the environment or process conditions in which the polymerization reactions occur introduce more sub-classes of polymers. For example, step-growth reactions may take place as *melt phase*, *solid-state*, *solution*, or *interfacial* polymerization:

- Melt-phase processes are carried out above the melting point of the polymer
- Solid-state processes are carried out below the melting point of the polymer
- Solution processes are carried out in the presence of an inert solvent
- Interfacial processes are carried out in the interface between an organic phase and an aqueous phase

*Chain Growth Reaction Sub-classes*

Chain-growth polymerization may take place in *bulk phase*, *solution, precipitation*, *suspension*, or *emulsion*:

- Bulk polymerization is carried out in the bulk monomer phase without a solvent
- Solution polymerization is carried out in the presence of an inert solvent in which monomers and polymer are dissolved
- Precipitation polymerization is carried out using a solvent to precipitate out the polymer
- Suspension polymerization involves monomers suspended as droplets in a continuous phase (usually water) to which an oil-soluble initiator is added
- Emulsion polymerization involves monomers and micelles dispersed in a continuous water phase using surfactants. Initiator is added to the emulsion of partially water soluble monomers in the surfactant solution

There are additional process related classifications that have to do with reactor geometry. These are discussed in sections covering unit operation modeling later in this User Guide.

# POLYMERS PLUS REACTION MODELS

There are two types of reaction models available in Polymers Plus:

- Built-in models
- User models

## Built-in Models

The polymerization reaction models available in Polymers Plus are summarized in Table 4.5. In addition to models for the chemistries and process types discussed, there is one model available for generic polymer modification reactions. This model follows a standard power-law scheme and is used to represent reactions involving modifications to segments of polymers made through one of the conventional reaction schemes. One of the standard Aspen Plus reaction models can also be used in conjunction with the polymerization reaction models. These models are listed in Table 4.6.

For more information about these models, consult the *Aspen Plus User Guide* and *Aspen Plus User Models*.

***Table 4.5 Polymers Plus Polymerization Reaction Models***

| Model Name | Chemistry | Processes | Polymers |
|---|---|---|---|
| **Step-growth** | | | |
| STEP-GROWTH | Condensation | Melt phase | PC, PBT, PET, Nylons |
| **Chain-growth** | | | |
| FREE-RAD | Free-radical | Bulk, solution | PS, PVAC, SAN, PMMA |
| EMULSION | Free-radical | Emulsion | SBR, SBA |
| ZIEGLER-NAT | Ziegler-Natta / metallocene coordination complex | Bulk, solution | HDPE, PP, LLDPE |
| IONIC | Anionic/Cationic group transfer | Solution | PIB, SBR, PEO |
| **Generic** | | | |
| SEGMENT-BAS | Standard power-law | N/A | PVA from PVAC |

***Table 4.6 Aspen Plus Standard Reaction Models***

| Model Name | Description |
|---|---|
| LHHW | Langmuir-Hinshelwood-Hougen-Watson reaction rate expressions |
| POWERLAW | Power-law reaction rate expressions |
| USER | Kinetic rate expressions supplied by user, kinetic rate computed in user supplied subroutine |

## User Models

There are cases where the built-in models do not provide the features necessary to model specific polymerization kinetics. Some of the polymerization reaction models provide capabilities to incorporate user reactions. In addition, the USER reaction model provides the capability for defining user kinetic schemes.

The USER reaction model is structured to allow the specification of the reaction stoichiometry. In addition, there are vectors for entering user real and integer parameters. This input information along with the reaction vessel contents, in the form of the stream structure, is made available to a user supplied Fortran subroutine during calculations.

Note that component attributes are part of the stream structure. There is an update and initialization scheme to automatically process these attributes. The user supplied Fortran subroutine can return rates for components and component attributes.

From the subroutine, Aspen Plus utilities including physical property routines, math utilities, and stream handling utilities can be accessed. Some of these utilities are documented in Appendix H.

# REFERENCES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# 4.1 STEP-GROWTH POLYMERIZATION MODEL

This section covers the step-growth polymerization model available in Polymers Plus. It begins with general background information on step-growth polymerization and covers some of the terms associated with these kinetics. Several industrial polymerization processes are examined in detail. A discussion of the model features and usage is also included.

Topics covered include:

- Summary of Applications
- Step-Growth Processes
- Reaction Kinetic Scheme
- Model Features and Assumptions
- Model Structure
- Specifying Step-Growth Polymerization Kinetics

The *Polymers Plus Examples & Applications Case Book* illustrates how to use the step-growth model to simulate nylon-6 polymerization from caprolactam.

# SUMMARY OF APPLICATIONS

Step-growth polymerization can be used to model various polycondensation and specialty plastic processes. Some of the applicable polymers are described below:

- Aliphatic polycarbonates - Transesterification of diols with lower dialkyl carbonates, dioxolanones, or diphenyl carbonate in the presence of catalysts such as alkali metal, tin, and titanium compounds.
- Aromatic polycarbonates - Reaction product of bisphenols with carbonic acid derivatives. May be prepared by transesterification, solution polymerization, and, most often by interfacial polymerization.
- Polyesters - Produced commercially in two steps: monomer formation by ester interchange of diesters with diols or esterification of diacids with diols, followed by polycondensation by removing excess diols to promote chain extension. This is accomplished commercially on a simple two-vessel batch process or on large-scale multi-vessel continuous-polymerization process.
- Polyamides - Produced via direct amidation, reaction of acid chlorides with amines, ring-opening polymerization, reaction of diacids and diisocyanates, etc. Commercially prepared by melt polycondensation, ring-opening polymerization, and low temperature solution polymerization.
- Polyurethanes - Polyurethane isocyanates are usually produced commercially by the phosgenation of amines. Polyester polyols are prepared by step-growth polymerization.

# STEP-GROWTH PROCESSES

Several commodity polymers, including polyesters, nylons, and polycarbonate, are manufactured through step-growth polymerization processes. This section examines some of the major processes which can be represented using the step-growth polymerization kinetics model.

## Polyesters

### Continuous Polyethylene-Terephthalate Processes

Polyethylene-terephthalate (PET) is produced by the step-growth polymerization of ethylene glycol, a diol, and either terephthalic acid, a diacid, or dimethyl terephthalate, a diester. Most processes are continuous although many older process lines operate in batch or semi-batch mode.

*Direct Esterification*

The direct esterification process, shown in Figure 4.1, involves the reaction of ethylene glycol with terephthalic acid. The terephthalic acid is mixed with excess ethylene glycol to form a solid-liquid paste. In the continuous process, the monomer paste is typically fed to a well-mixed reactor, the primary esterifier, which operates at temperatures of 250-290 °C and pressures ranging from one to several atmospheres. Typical residence times range from one to four hours in this stage of the process.

A solid at room temperature, terephthalic acid has limited solubility in the polymer solution, even at the relatively high process temperatures. Further, the dissolution rate of TPA may be limited by the solid-liquid mass transfer rate, especially if the average particle size is large, or when the reactor operates at high temperatures and pressures.

*Secondary Esterification*

In most continuous plants, the primary esterifier is followed by secondary and, occasionally, a tertiary esterifier. These reactors range from single-tank CSTRs to a variety of multiple-stage CSTRs composed of vertical or horizontal vessels divided into two or more chambers by partitions. Secondary esterification reactors typically have residence times on the order of an hour, with temperatures similar to or slightly higher than the primary esterifier. The secondary esterification reactor is often run under atmospheric conditions, although slight positive pressure or vacuum pressures are also used in some processes.

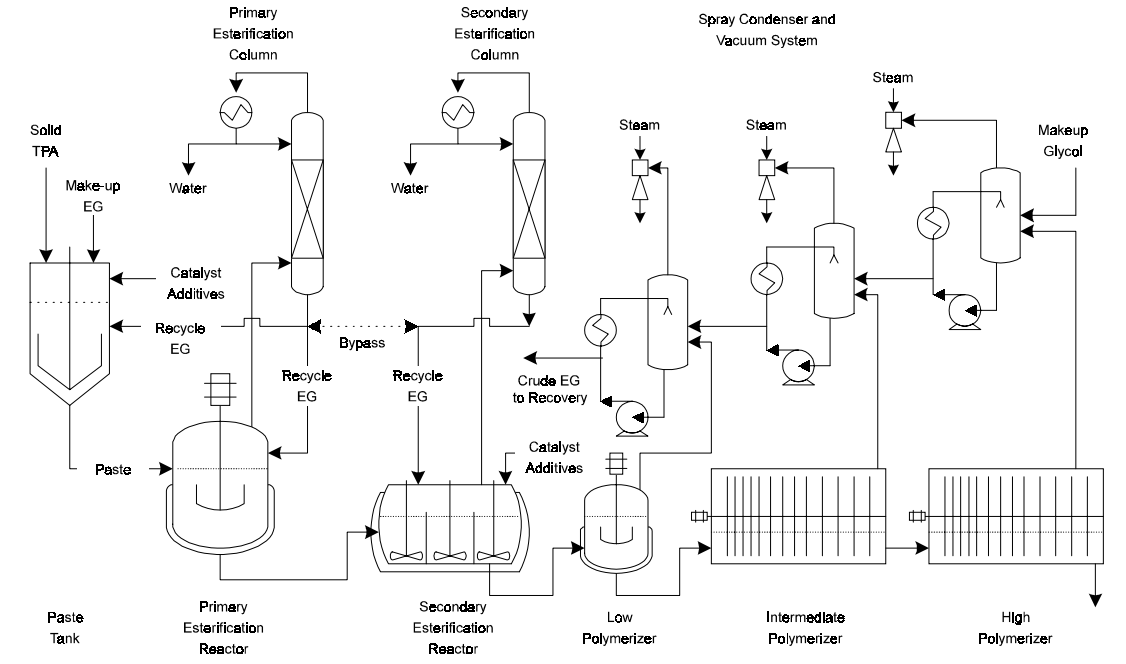



***Figure 4.1*** *Continuous Direct Esterification Process for PET*

Vapor from the esterification reactors flows to one or more distillation columns which separate ethylene glycol from the reaction by-products which include water and acetaldehyde. In some processes, spray-condenser loops are used to "wash" entrained TPA and vaporized low-molecular weight oligomers from the vapor stream to prevent oligomer build-up in the distillation columns.

*Glycol Recovery*

The ethylene glycol from the esterification distillation columns can be recycled directly to the esterification reactors, to the paste mixing tank, or, in the case of high-quality products, it can be collected for further processing to remove contaminants. The companies which license PET technology use a wide variety of glycol recovery and recycling schemes. All of these recycling schemes can be simulated using conventional distillation, flash, and heat exchanger models available in Aspen Plus.

*Esterification Results*

The product of the esterification reactors is composed of short-chain oligomers with some residual monomers. The main oligomer in the product is bis-hydroxyethyl-terephthalate (BHET), which is slightly volatile under typical operating conditions. The step-growth model includes an "oligomer" feature which can be used to account for evaporative loss of linear oligomers such as BHET.

*Transesterification Process*

In the transesterification process, dimethyl terephthalate (DMT) is used instead of terephthalic acid (TPA). One advantage of this process is the relatively high solubility of DMT, which eliminates the solid-liquid mass transfer problem in the first stage of the process. A second advantage is the low acidity of DMT, which reduces several of the side reaction rates and results in a higher quality polymer. The limitations of the transesterification process include increased monomer cost, production of methanol as a by-product (instead of water), and reduced reactivity in the finishing stages.

The transesterification process produces methanol as a reaction by-product. The methanol is distilled from ethylene glycol through distillation columns. Recovered glycol may be recycled to the reactor, the paste mixing tank, or accumulated for additional processing.

It is desirable to minimize the concentration of methylester ends in the feed to the polymerization section. Obtaining high conversions is very important in the DMT process because the reverse reaction of methanol with PET is more highly favored than the reaction of water and PET. A wide variety of proprietary reactors are used to effect high end-group conversion during the transesterification process.

*Continuous Polymerization*

The continuous polymerization process is the same for the direct esterification and transesterification processes. Typically, the polymerization section consists of one or more CSTR reactors (pre-polymerization reactors) followed by one or more horizontal "finishing reactors" (polymerization reactors). These reactors consist of a series of rotating blades or disks which lift polymer from a pool at the bottom of the reactor into a vapor space over the pool. The design criteria of these reactors are to maximize surface area generation while minimizing back-mixing. In polyester processes, the finishing reactors are almost always limited by the liquid-vapor mass transfer rates. In some cases, the pre-polymerization reactors are also limited by mass transfer.

The reactors in the polymerization section operate at increasingly higher temperatures and lower pressures to enhance the devolatilization of excess glycol and reaction byproducts such as water, methanol, and acetaldehyde. Reactor residence times range from thirty minutes to four hours depending on the number and type of reactors in the polymerization section.

Vapor from the polymerization section is scrubbed by spray-condenser loops composed of a contacting vessel, accumulation tank, pump, and heat exchanger. In most plants, vacuum is generated through venturi jets operated by steam or vaporized glycol. In some process configurations, the condensed glycol and water mixture is recycled to the esterification columns. Otherwise, the condensate is accumulated and processed to recover glycol.

*Operating Conditions*

The esterification and transesterification sections of PET processes frequently operate below the melting point of the polymer. Under these operating conditions, the process can be considered solution polymerization. The polymerization reactors operate above the melting point of the polymer in a true melt-phase polymerization. The step-growth reaction model may be used for both modes of operation. In most cases, the same reaction kinetics apply to both solution- and melt-phase reaction processes.

*Final Products*

The continuous melt-phase PET processes generally produce polymer with an average intrinsic viscosity of approximately 0.6 dl/g, which corresponds to a number-average degree of polymerization near 100 units. This product may be directly spun as clothing fiber, partially oriented yarn (POY), film, or it may be cooled and chipped for on- or off-site use.

Recent increases in consumer recycling programs and consumer preference for unbreakable bottles has created a very large market for polyester bottles. These bottles are molded from a higher molecular weight polyester chip which is produced by a solid state process. Fundamentally, the step-growth model can apply to solid-state polymerization. However, at this time, Polymers Plus does not include a solid-state polymerization (SSP) reactor model. Semi-rigorous SSP models can be developed using a series of CSTR reactors. Solid phase polymer solutions can be treated as a liquid phase in Polymers Plus. The property system switches between liquid-phase property models and solid-phase property models when the temperature drops below the melting point of the polymer component.

## Batch Polyethylene-Terephthalate Processes

Polyethylene Terephthalate is also produced in batch and semi-batch processes, as shown in Figure 4.2. Usually, the process consists of two batch reactors in series. The role of the first reactor is to reach high conversions of the terephthalate monomer while minimizing undesirable side reactions. The role of the second reactor is to raise the molecular weight of the polymer to appropriate levels.

The first reactor is coupled to a column which separates the volatile reaction by-products from excess ethylene glycol and evaporated oligomers. The heavy components are continuously returned to the reactor during most of the batch cycle. Towards the end of the cycle, the evaporated ethylene glycol and residual monomers are removed and accumulated for re-use in the next batch.

The batch esterification process commonly uses a semi-continuous feeding system for the solid TPA. In most batch esterification processes, the reaction rate is limited by the rate of dissolution of TPA. This is complicated by the relationship between the mass transfer rates and particle size.

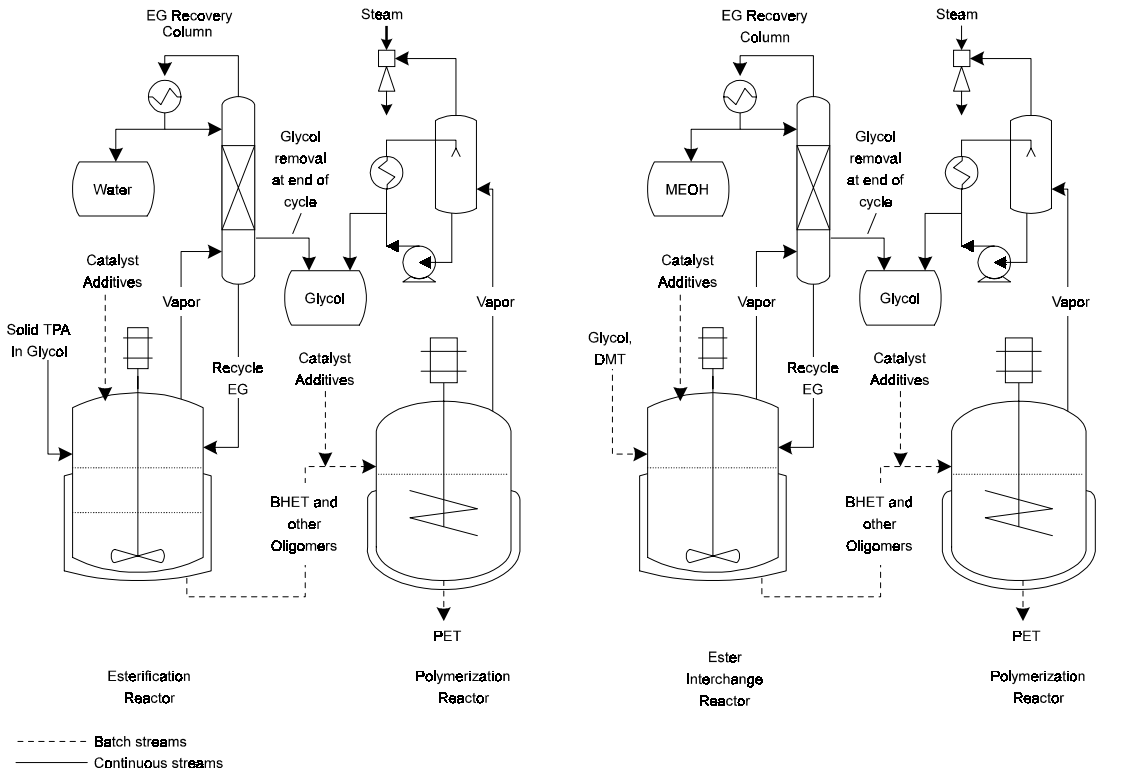



***Figure 4.2*** *Batch / Semi-Batch PET Processes*

To enhance TPA solubility, a portion of the polymer product is retained in the reactor at the end of the cycle. The recycled product is used to start the next batch. This design allows the cycle to start at a higher temperature, reducing the cycle time for each batch. The trade off between the batch cycle time and the quantity of recycle polymer is one of the most interesting problems to examine using simulation technology.

The batch transesterification process is typically operated in true-batch mode, without recycling polymer. In this process, the monomers, ethylene glycol and DMT, are charged to the reactor at the beginning of the cycle. The continuous removal of methanol from the batch reactor makes very high end-group concentrations possible.

This version of Aspen Plus does not include an appropriate reactor model to simulate batch polymerization reactors with overhead distillation columns. AspenTech's Polyester Technology Package includes several modeling solutions for representing these types of batch processes in the Aspen Plus and Aspen Custom Modeler environments.

*Second Batch Stage*

The liquid product from the batch esterification or transesterification is charged to a second batch stage. In this stage, the reactor is evacuated as the temperature is increased. These operating profiles enhance the removal of excess ethylene glycol from the reaction mixture, allowing these highly reversible reactions to proceed.

As the polymer viscosity increases, the reactions become limited by the rate of mass transfer from the liquid phase to the vapor phase due to decreased surface renewal rates and reduced agitator speeds.

## Other Polyester Processes

Polybutylene-terephthalate (PBT) is an engineering plastic frequently used for machine parts, car body panels, and other applications. Polybutylene terephthalate is analogous to PET, except butylene glycol is used in place of ethylene glycol. Most PBT is manufactured from DMT through continuous transesterification processes, although batch processes and direct esterification processes are also found in industry.

In the PBT process, tetrahydrofurane, THF, is formed from butylene glycol end groups as an undesirable reaction by-product. The transesterification process is favored over direct esterification because the acid end groups in TPA catalyze the formation of THF.

Polypropylene-terephthalate (PPT) is used for carpet fiber and other applications. Like PET and PBT, PPT can be manufactured from terephthalic acid or dimethyl terephthalate. In the PPT process, propylene glycol is used as the diol monomer.

Polyethylene-naphthalate (PEN) manufacturing processes are under development by several polyester producers. This new product has a higher melting point than PET, and is aimed at specific demands, such as hot-fill bottles, which are not well satisfied by other polyesters. The dimethyl ester naphthalate monomer is much more expensive than TPA or DMT, so PEN is frequently produced as a copolymer with PET.

At this time, most PEN is produced in batch processes which are analogous to the batch PET process. Copolymers of PEN and PET are being used for some bottling applications already. The similarities in the chemical mechanism for PET and PEN make them relatively easy to copolymerize in various ratios, resulting in several product grades with properties intermediate between pure PET and pure PEN.

## Polyester Technology Package

Aspen Technology has several offerings to provide solutions for polyester processes, including a Polyester Technology Package for steady-state and dynamic simulation of melt-phase continuous or batch polyester processes. Consulting, training, and turn-key solutions are also available. The Polyester Technology Package is designed for PET, but can be easily modified for analogous polyesters such as PEN, PBT, etc.

The models in the package account for all the major side reactions in the process, such as thermal scission, aldehyde formation, DEG formation, and cyclic trimer formation. The reaction kinetic models consider the influence of several common catalysts and additives as well as acid catalysis and uncatalyzed side reactions. The package includes reactor models which consider solid-liquid mass transfer for the direct esterification process, and liquid-vapor mass transfer limited kinetics for the polymerization reactors.

The Polyester Technology Package includes models of several common process configurations, including both batch and continuous processes. The models predict various quality parameters such as the acid end group concentration (acid value), intrinsic viscosity, vinyl end content, DEG content, conversion, etc.

Contact your Aspen Technology sales representative for more information about the Polyester Technology Package or available consulting services.

## Nylon-6

Nylon-6 is produced by ring-opening polymerization of ε-caprolactam. Water and caprolactam are fed to a primary reactor where the ring-opening reaction takes place. The primary reactor may be a single (liquid) phase tubular reactor, CSTR, or one of a variety of proprietary reactors.

*VK Column*

One of the most well known of these proprietary designs is the Vereinfacht Kontinuierliches (or VK) column. The VK column is a reactor with a high aspect ratio which is filled to relatively high liquid levels (Figure 4.3). The reacting mixture boils vigorously near the top of the VK column, resulting in considerable radial and axial mixing. Below this well-mixed zone is a plug-flow zone in which the hydrostatic pressure is sufficient to suppress boiling. Reactors of this type can be simulated using one or more two-phase CSTR reactors (model RCSTR) in series with a single liquid-phase plug flow reactor (model RPLUG).

The top of the VK column typically operates near atmospheric pressure. Heat exchangers inside the upper section of the reactor bring the reactants to temperatures of 220-270°C. Typical residence times are in the order of three to five hours. A reflux condenser or distillation column over the reactor returns the monomer and most of the water back to the VK column.

Although the initial stages of Nylon-6,6 polymerization are catalyzed by water, the water must be removed in later stages to allow the condensation reactions to proceed to high conversion. Water removal is accomplished by carrying out the reaction in a series of stages at successively lower pressures. Secondary stages typically involve one or more CSTR reactors followed by vertical wiped-film evaporators. Inert gas may be used to strip water from the polymer melt.

For some products, chain terminators are used to control the molecular weight of the product. Acetic acid is commonly used, but any monofunctional acid or alcohol can be used to control molecular weight build-up.

Horizontal finishing reactors may be used to increase the polymer molecular weight and reduce the residual monomer and cyclic oligomer concentrations. In these devolatilization stages, the evaporation of water, excess caprolactam, aminocaproic acid, and cyclic oligomers is limited by the rate of mass transfer from the liquid phase to the vapor phase.

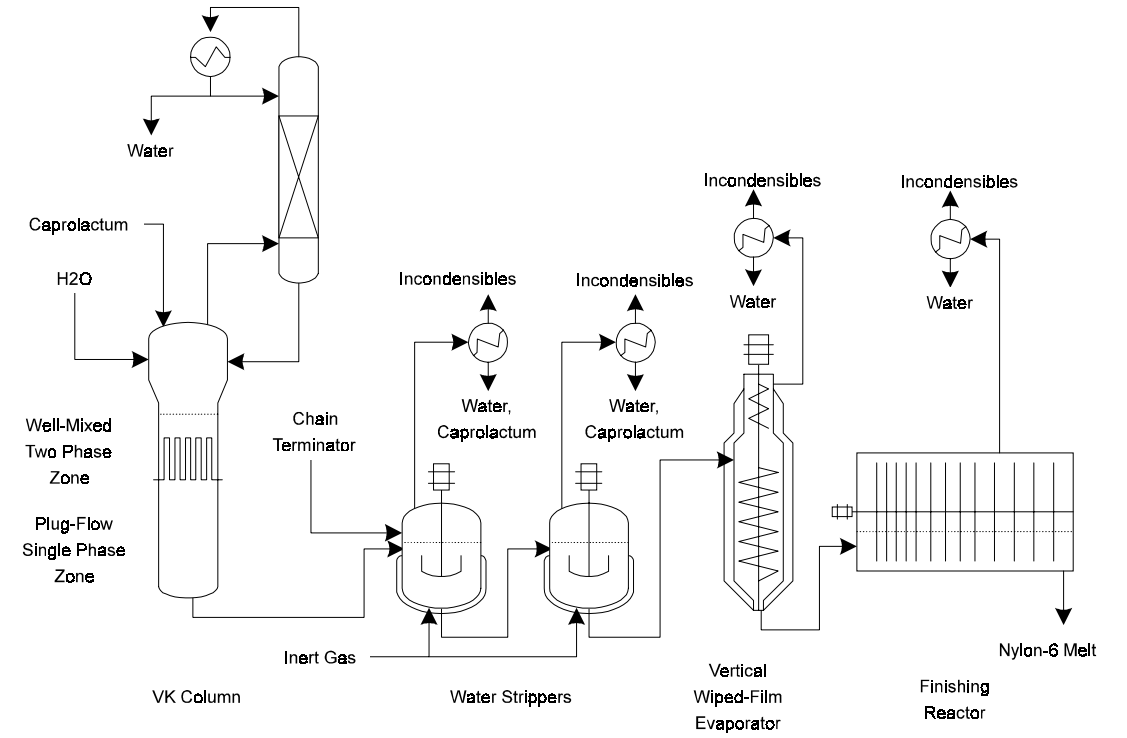



***Figure 4.3*** *Continuous Melt-Phase Nylon-6 Process*

## Nylon-6,6

Nylon-6,6 is manufactured by two types of processes. In the most common process, dyadic nylon salt is first produced by mixing adipic acid (ADA) in an aqueous solution of hexamethylene diamine (HMDA). A newer process involves the direct melt polymerization of the two monomers.

### Salt Preparation

In the traditional salting process, the formation of nylon salt ensures stoichiometric ratios of the two monomers, allowing the production of high molecular weight polymers. In the salt solution process, solid adipic acid is dissolved in an aqueous solution of HMDA. The resulting aqueous salt solution is concentrated by further addition of the monomers and/or by partial evaporation.

An alternative salting process uses methanol as the primary solvent. Solutions of adipic acid and HMDA in methanol are prepared separately in continuously stirred heated tanks. These solutions are mixed in a reactor where the nylon salt is generated. Most of the nylon salt precipitates out of solution due to the low solubility of the nylon salt in methanol. A small amount of the salt, however, remains dissolved in the reactor, resulting in the generation of some short-chain oligomers. The salt slurry is centrifuged to remove the solid salt. Methanol is used as a washing solution in the centrifuge to further purify the salt. The methanol is purified in a distillation column and recycled. The solid nylon salt is dried and collected for use on- or off-site.

## Polymerization from Aqueous Salt Solutions

Most nylon-6,6 is produced in continuous processes made up of several stages. The primary stage operates at high pressures and temperatures to control the loss of volatile monomers and to accelerate the reactions. In the intermediate reactors, the operating pressure is reduced substantially and much of the excess water is evaporated. The finishing stages of the process are made up of one or more wiped-film evaporators which help to remove the remaining residuals. A typical nylon-6,6 process is shown in Figure 4.4.

*First Stage*

In the first stage, aqueous salt solutions are fed to a reactor which operates at high temperatures (230-290°C) and pressures (> 250 psig). High temperatures are required to dissolve the salt and to accelerate the reaction rates. The high pressure is required to avoid excess loss of HMDA, which is generated by polymerization reactions. In the first reactor, the nylon salt dissolves and condensation reactions take place between molecules of the dissolved salt and between the dissolved salt and polymer end groups. Much of the water which enters with the salt and is generated by the condensation reactions is boiled off in the first stage due to the high operating temperature.

In some processes, the salt solution is fed to a column over the first reactor. As the solution flows down the column, excess water is driven off. Condensation reactions take place in the reactor at the bottom of the column as well as in the trays of the column. The column also condenses evaporated HMDA, returning it to the reactor vessel. Additives, such as titanium dioxide, are fed to the primary reactor vessel.

The reactor vessel is made up of two parts: a separation vessel and a heat exchanger tube-bank. The separator vessel is located at the bottom of the column, where it receives the reflux from the column. The liquid at the bottom of the separator is pumped through the tube-bank heat exchanger, which acts as the reboiler for the column. The high circulation rates through the heat exchanger section of the reactor keep the reactor contents well mixed.

*Intermediate Stage*

Liquid from the primary reactor must be throttled to lower pressures to remove water, which allows the reversible condensation reaction to proceed to higher conversions. The depressurization and devolatilization of the intermediate are carried out by several different techniques involving a series of degassing vessels connected by throttle valves. In some processes, a loop-type reactor is used to reduce the pressure.

Excess HMDA or adipic acid or monofunctional chain stoppers, such as acetic acid, may be added in the intermediate stages of the process to control the molecular weight build-up. Catalysts and thermal stabilizers are also added to the oligomer.

*Final Stage*

In the final stages of polymerization, wiped-wall evaporators are used to finish the reaction at high temperatures (up to 300°C) and medium vacuum pressures (760-200 torr). Typical finishing reactor residence times range from 20-60 minutes. The removal of water and excess monomers from the liquid phase may be limited by the mass transfer rate.

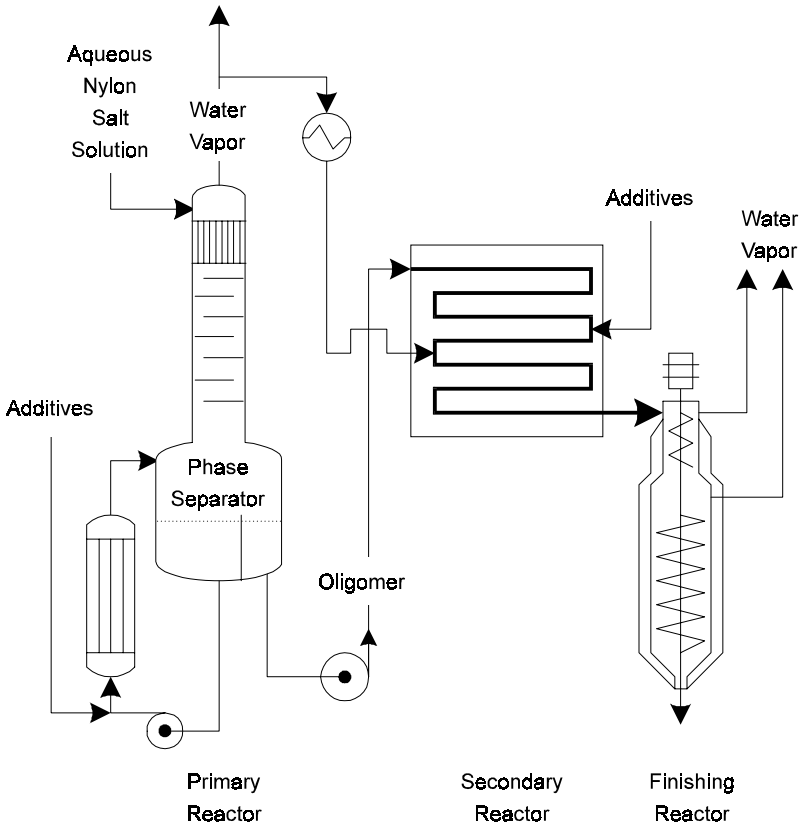



***Figure 4.4*** *Continuous Process to Produce Nylon 6,6 from Nylon Salt*

### Melt-Phase Polymerization

Recent developments in nylon-6,6 polymerization have led to the development of continuous melt-phase polymerization processes. Adipic acid and hexamethylene diamine solutions are fed to a tubular primary reactor, which operates at very high pressures (approximately 1000 psig), temperatures around 275°C, and residence times of 15-30 minutes. Under these conditions, boiling does not occur in the reactor.

The pressure is throttled down to 250-350 psig through a series of valves or tubes of successively larger diameter. The pressure profile must be adjusted to minimize cooling caused by the rapid evaporation of steam, which can cause the polymer solution to freeze.

In the final stage, the polymer is brought close to chemical equilibrium (with dissolved water and excess monomers) in a wiped film evaporator.

## Polycarbonate

Polycarbonate is a relatively strong polymer with good optical and mechanical properties. It is used in several applications including car body parts (frequently blended with PBT), specialty films, and laser disc media.

Historically, most polycarbonate was produced by interfacial polymerization of bisphenol-A (BPA) with phosgene. In the interfacial process, the reactions are relatively fast, but the reaction rate is limited by the mass transfer rates of the reactants from the bulk liquid phases into the swollen polymer phase.

A limited amount of polycarbonate is produced from BPA and phosgene in a solution polymerization process. The reaction is carried out by solution polymerization in pyridine. The pyridine solvent captures chlorine from the phosgene groups, resulting in pyridine chloride as a reaction by-product.

Recently, the melt-phase polymerization of bisphenol-A with diphenyl carbonate (DPC) has become an important industrial process. The melt polymerization process has a significant safety advantage over the interfacial process because phosgene is highly volatile and extremely toxic. Figure 4.5 shows a typical melt-phase polycarbonate process.

The monomers, BPA and DPC, are fed in a carefully controlled ratio to a series of CSTRs. Phenol, which is generated as a reaction by-product, is vaporized in the reactors and must be condensed and recycled. Distillation columns are used to recover residual monomers from phenol.

The CSTRs are followed by a series of wiped film evaporators and horizontal finishing reactors which operate at successively lower pressures to enhance the removal of residual monomers and phenol. These reactors are limited by the mass transfer rate of phenol from the melt.

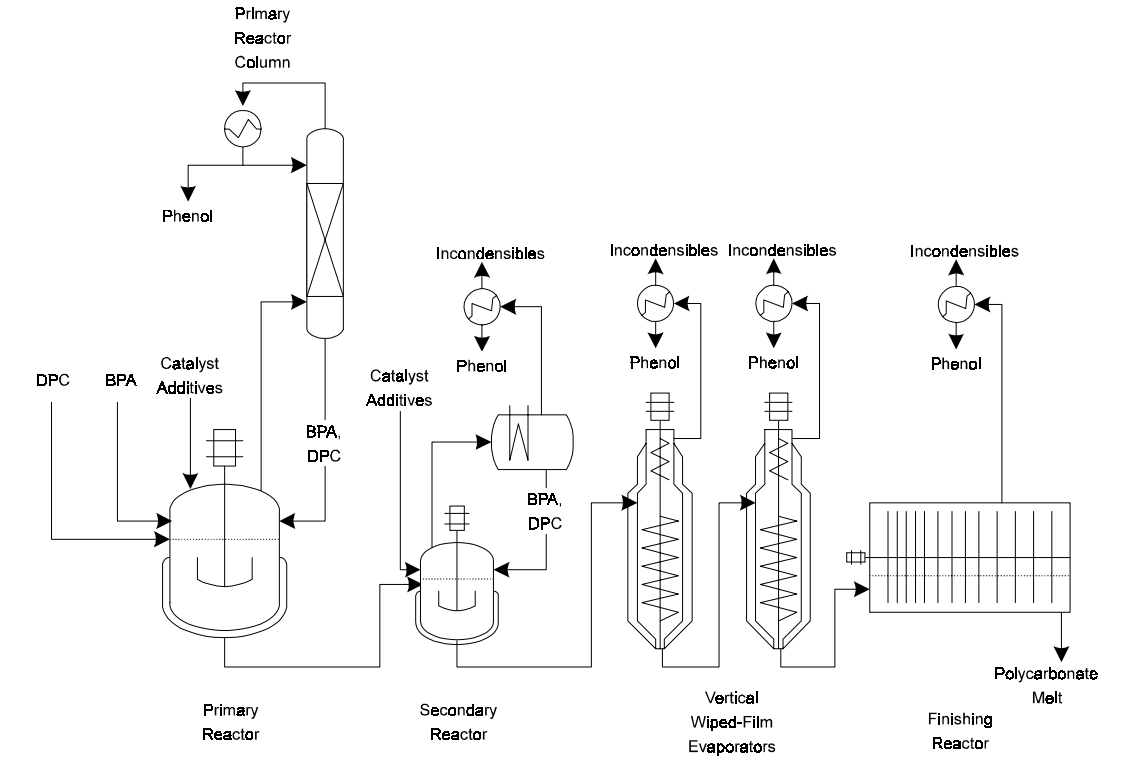



***Figure 4.5*** *Continuous Melt Polycarbonate Process*

# REACTION KINETIC SCHEME

## Overview

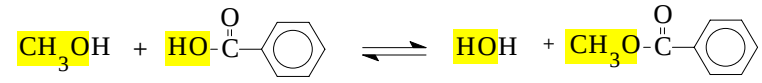
### Nucleophilic Reactions

Step-growth polymerization involves reactions between monomers containing *nucleophilic* and *electrophilic* functional groups. Nucleophilic groups are electron-strong groups, typically alcohols (~OH), amines (~$NH_2$), or water. Electrophilic groups are electron-weak groups such as acids (~COOH), esters (~COO~), amides (~CONH~), and isocyanates (~NCO). When two chemical species react, the species with the strongest nucleophilic group is called the *nucleophile*; the other reactant bearing the strongest electrophilic group is called the *electrophile*.

Nucleophiles and electrophiles participate in bimolecular reactions. Depending on the types of functional groups in each reactant, the reaction mechanism may be *nucleophilic substitution* or *nucleophilic addition*.

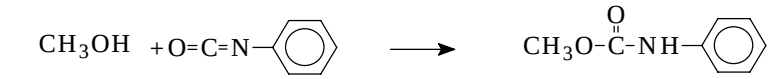
*Nucleophilic Substitution*

In nucleophilic substitution reactions, a nucleophilic group from one reactant (the nucleophile) displace a nucleophilic group in the other reactant (the electrophile), resulting in two new products. (Note: Electrophilic groups are highlighted in each of the following figures.) Nucleophilic substitution reactions tend to be highly reversible.




*Nucleophilic Addition*

In nucleophilic addition reactions, the electrophile and nucleophile combine to form a new functional group. These reactions are typically irreversible.




Currently, the step-growth reaction generation algorithm is limited to condensation reactions. Pseudocondensation reactions must be defined through the user reaction feature.

In some reverse reactions and re-arrangement reactions, the electrophile may be a polymer or oligomer. These reactions occur at the bonds which link two segments together. To fully describe these reactions, the two segments in the electrophile must be identified. In this case, we refer to the electrophile as the "victim" reactant and the nucleophile as the "attacking" reactant. The victim reactant includes a nucleophilic segment and an electrophilic segment.

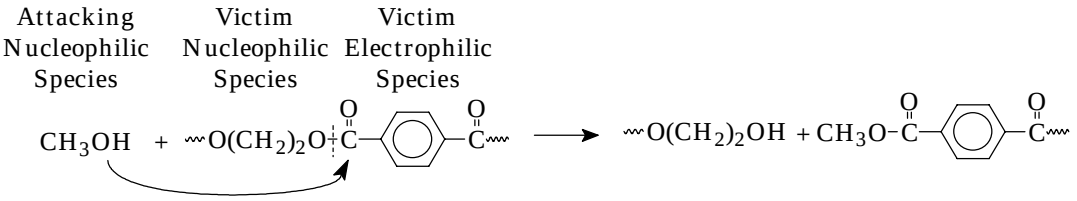



Table 4.8 lists the role of electrophiles and nucleophiles in several step-growth polymerization processes. The table lists the reacting functional groups, the characteristic repeat unit, and the by-product related to each polymerization process.

### *Table 4.8 Typical Step-Growth Reactants and Products*

| Polymer Class | Nucleophile | Electrophile | Repeat Unit | Condensate By-product |
|---|---|---|---|---|
| Polyester | ~OH | ~COOH | ~(C=O)O~ | $H_2O$ |
| | ~OH | ~$COOCH_3$ | ~(C=O)O~ | $CH_3OH$ |
| | ~O(C=O)$CH_3$ | ~COOH | ~(C=O)O~ | $CH_3COOH$ |
| Polyamide | ~$NH_2$ | ~COOH | ~(C=O)NH~ | $H_2O$ |
| Polyacetal | ~OH | ~O(C=O)Cl | ~O(C=O)O~ | HCl |
| (Polycarbonate) | ~OH | ~O(C=O)Oph | ~O(C=O)O~ | PhOH |
| Polyurethanes | ~$NH_2$ | ~(C=O)Cl | ~NH(C=O)O~ | HCl |
| | ~OH | ~N=C=O | ~NH(C=O)O~ | none |
| Polyurea | ~$NH_2$ | ~N=C=O | ~NH(C=O)NH~ | none |
| Polyether | ~OH | ~CH-$CH_2$ (O) | ~$OCH_2C(OH)H$~ | none |

## Reaction Nomenclature

Polymerization reactions are classified by chemical mechanism, by the number of reacting components, and by the influence a reaction has on the chain length distribution. This section describes the basic types of reactions found in step-growth polymerization and serves as a glossary of reaction nomenclature.

*Intermolecular* reactions involve two or more molecules.

*Intramolecular* reactions involve two sites on the same molecule.

*Condensation* reactions arepolymerization reactions which produce a small molecule as a by-product. Typically, the condensate is a volatile compound such as water, methanol, acetic acid, or phenol. Step-growth reactions involving chlorine end groups result in hydrochloric acid or chlorinated hydrocarbon condensate products.

*Reverse condensation* reactions are where condensate molecules cleave an existing polymer chain, producing two smaller chains. Reverse condensation reactions near the end of a polymer molecule can generate free monomers.

*Pseudocondensation* reactions are nucleophilic addition reactions. These reactions involve rearrangement of atoms in two different functional groups, resulting in a new functional group. No by-products are produced by pseudocondensation reactions. Pseudocondensation reactions can involve two monomers, a monomer and a polymer end group, or two polymer end groups.

*Addition* reactions are reactions in which small molecules, including free monomers, dyadic salts, and cyclic monomers and dimers react with the end of a growing polymer molecule. These reactions are responsible for the conversion of the monomers and most of the conversion of functional end groups.

*Combination* reactions involve reactions between the end groups of two polymer molecules. In most systems, combination reactions play an important role in molecular weight growth.

*Rearrangement* reactions occur between two polymer molecules, resulting in two new polymer molecules with different molecular weights. These reactions may involve the end group of one molecule and an internal site on another molecule, or they may involve internal sites on both molecules.

*Ring opening* reactions are intermolecular reactions between condensate or monomer molecules and cyclic monomers or oligomers. Condensate molecules or monomers react with cyclic compounds, opening the ring structure to produce linear oligomers or cyclic monomers.

*Ring closing* reactions are intramolecular reactions which occur between the two end groups of a linear molecule. Ring-closing reactions which occur between two end groups of a branched or network molecule are referred to here as *intramolecular cyclization* to differentiate them from reactions which form ring-shaped molecules.

*Ring addition* reactions are intermolecular reactions between polymer end groups and cyclic monomers or oligomers. The end group of the polymer links to the cyclic compound, opening the ring and lengthening the chain of the linear molecule.

*Cyclodepolymerization* reactions are intramolecular reactions in which a polymer end group reacts with a segment in the same molecule, forming a ring. The ring-shaped molecule is lost from the linear parent molecule, reducing the molecular weight of the parent.

*Terminal monomer loss* involves the loss of a monomer unit at the end of a polymer chain due to thermal degradation mechanisms.

*Random scission* involves the spontaneous cleavage of a polymer chain due to thermal degradation.

*End group reformation* reactions are those reactions which convert one type of end group into another without influencing the chain length.

Table 4.9 summarizes the reactions schematically.

### *Table 4.9 Overview of Reactions in Step-Growth Polymerization*

| Reaction Class | Reaction Mechanism | Reaction Type | Reaction Scheme | Included |
|---|---|---|---|---|
| Intermolecular | Nucleophilic Substitution | Condensation - Monomer Addition | $M + M \rightarrow P_2 + W$ | Yes |
| | | | $P_n + M \rightarrow P_{n+1} + W$ | Yes |
| | | Condensation - Polymer Addition | $P_n + P_m \rightarrow P_{n+m} + W$ | Yes |
| | | Reverse Condensation - Terminal Monomer Loss | $W + P_2 \rightarrow M + M$ | Yes |
| | | | $W + P_n \rightarrow P_{n-1} + M$ | Yes |
| | | Reverse Condensation - Scission | $W + P_n \rightarrow P_{n-m} + P_m$ | Yes |
| | | Forward Polycondensation | $P_n + P_m \rightarrow P_{n+m-1} + M$ | Yes |
| | | Reverse Polycondensation | $M + P_n \rightarrow P_{n-m} + P_{m+1}$ | Yes |
| | | Re-arrangement | $P_n + P_m \rightarrow P_{n+m-q} + P_q$ | Yes |
| | | Ring Opening | $W + C_n \rightarrow P_n$ | No |
| | | Ring Addition | $P_n + C_m \rightarrow P_{n+m}$ | No |
| | Nucleophilic Addition (Pseudocondensation) | Monomer Addition | $M + M \rightarrow P_2$ | No |
| | | | $P_n + M \rightarrow P_{n+1}$ | No |
| | | Polymer Addition | $P_n + P_m \rightarrow P_{n+m}$ | No |
| Intramolecular | Pseudocondensation or Thermal mechanisms | Terminal Monomer Loss | $P_2 \rightarrow M + M$ | No |
| | | | $P_n \rightarrow P_{n-1} + M$ | No |
| | | Scission | $P_n \rightarrow P_{n-m} + P_m$ | No |
| | Nucleophilic Substitution | Ring-Closing | $P_n \rightarrow C_n + W$ | No |
| | | Cyclodepolymerization | $P_n \rightarrow P_{n-m} + C_m$ | No |
| | Nucleophilic Addition | Ring-Closing | $P_n \rightarrow C_n$ | No |

$P_n$ ***= linear polymer with n segments***

$C_n$ ***= cyclic polymer with n segments (***$C_1$ ***= cyclic monomer, such as caprolactam)***

***M = monomer***

***W = condensate***

## Polyester Reaction Kinetics

In the direct esterification process, polyesters are produced by the reaction of diols, such as ethylene glycol, with diacids, such as terephthalic acid. The esterification reactions generate one mole of water for each mole of ester groups formed. The reactions are catalyzed by acid end groups in the polymer and diacid monomer.

*Side Reactions*

Several of the key side reactions are also acid-catalyzed. In the PET process, these reactions include the formation of diethylene glycol, or DEG, from ethylene glycol. The transesterification process does not involve acids, and substantially less DEG is produced.

An analogous reaction generates tetrahydrofurane (THF) in the PBT process. Like DEG formation, THF formation is accelerated by acid end groups. Since THF poses environmental concerns, the generation of THF should be minimized. For this reason, PBT is usually produced by the transesterification route.

Metal acetate catalysts are used to accelerate the reaction rates in the later stages of the direct esterification process and throughout the transesterification process. These catalysts accelerate the main reactions and several side reactions including thermal scission and aldehyde formation.

In the transesterification process, acid end groups may be formed by thermal degradation reactions or by exchange reactions with water, which may be formed as a reaction by-product. These acid end groups participate in the reaction scheme, making transesterification kinetics a superset of esterification kinetics.

*Polymerization Stage*

The polymerization stage involves chain building reactions. There are two main growth mechanisms. Condensation reactions occur between two polymer end groups, releasing water or methanol. Polymerization reactions occur between diol end groups in different polymer molecules, generating a molecule of free glycol.

The polymer end group distribution and molecular weight distribution are randomized by redistribution reactions.

*Polyester Production Final Stages*

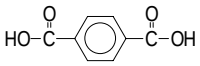
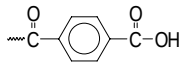
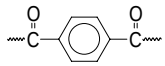
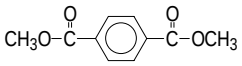
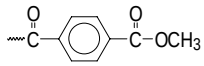
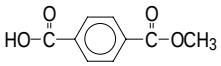
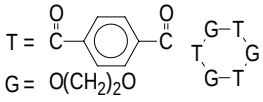
In the final stages of polyester production, high temperatures lead to thermal degradation reactions. In the PET process, these reactions degrade glycol end groups, producing acid ends and free acetaldehyde. Thermal scission reactions generate acid end groups and oxyvinyl end groups. Analogous reactions in the PBT process yield butenol and 1,4-butadiene. Additional side reactions involving these vinyl groups are the main source of color bodies in polyesters.

Cyclic compounds are formed by ring-closing and cyclodepolymerization reactions. Cyclic monomers, and some cyclic dimers do not form in terephthalic polyesters because of steric limitations. Trace amounts of larger cyclic oligomers, including trimers, tetramers, and pentamers, are commonly observed in terephthalate polyesters. These cyclic compounds reduce the quality of the polyester. Cyclic oligomers evaporate from the finishing reactors and condense in vapor vent lines, causing maintenance problems.

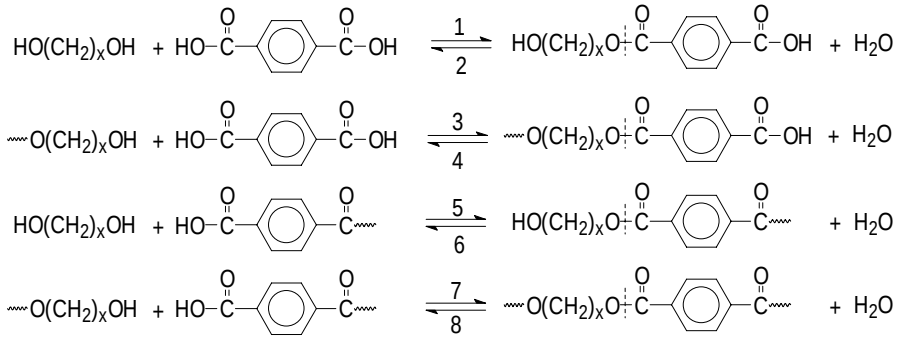
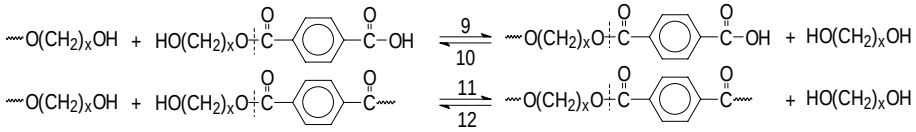
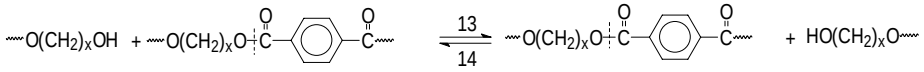
The reaction kinetics of terephthalate polyesters are summarized in the tables below. Table 4.10 documents the components involved in the reactions. Table 4.11 summarizes the step-growth reactions associated with terephthalate polyesters. For brevity, the table shows a subset of the reactions which actually occur - an analogous set of reactions involving DEG are also generated by the step-growth model. Table 4.12 describes how to assign rate constants to each of the reactions listed in Table 4.11.

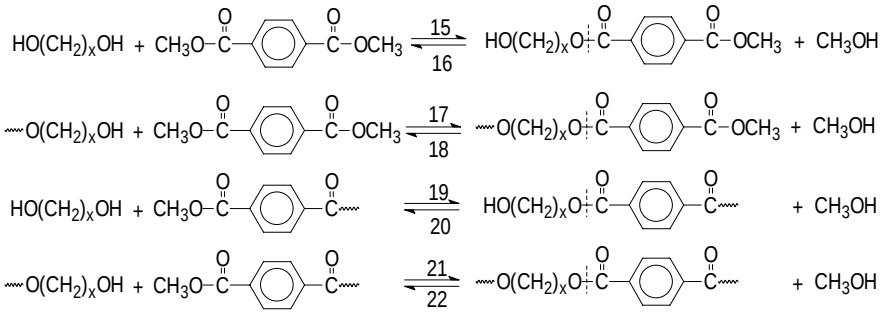
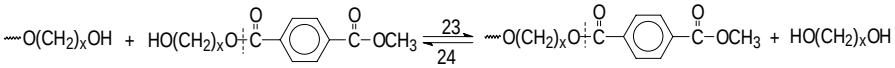
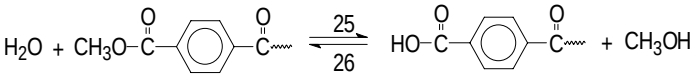
Many of the side reactions in the polyester process are not included in the reaction generation scheme, and must be added to the model as “user reactions”. These reactions are listed in Table 4.13. The recommended power-law exponents for the reactants in the side reactions are shown in Table 4.14.

## *Table 4.10 Components In Terephthalate Polyesters*

| Component ID | Databank ID | Component Structure | Component Name |
|---|---|---|---|
| TPA | C8H6O4-D3 |  | Terephthalic acid |
| T-TPA | C8H5O3-E |  | Terephthalic acid end group |
| B-TPA | C8H4O2-R |  | Terephthalate repeat unit |
| DMT | C10H10O4-D2 |  | Dimethyl terephthalate |
| T-DMT | C9H7O3-E |  | Dimethyl terephthalate end group |
| MMT | none |  | Monomethyl terephthalate |
| H2O | H2O | $H_2O$ | Water |
| MEOH | CH4O | $CH_3OH$ | Methanol |
| **Components In Polyethylene Terephthalate Processes** | | | |
| EG | C2H6O2 | $HO(CH_2)_2OH$ | Ethylene glycol |
| T-EG | C2H5O2-E | $\sim O(CH_2)_2OH$ | Ethylene glycol end group |
| B-EG | C2H4O2-R | $\sim O(CH_2)_2O\sim$ | Ethylene glycol repeat unit |
| DEG | C4H10O3 | $HO(CH_2)_2O(CH_2)_2OH$ | Diethylene glycol |
| T-DEG | C4H9O3-E | $\sim O(CH_2)_2O(CH_2)_2OH$ | Diethylene glycol end group |
| B-DEG | C4H8O3-R | $\sim O(CH_2)_2O(CH_2)_2O\sim$ | Diethylene glycol repeat unit |
| T-VINYL | C2H3O-E | $\sim OCH{=}CH_2$ | Oxyvinyl end group |
| C3 | none |  | Cyclic trimer |
| **Components In Polybutylene Terephthalate Processes** | | | |
| BD | C4H10O2 | $HO(CH_2)_4OH$ | 1,4 Butane diol |
| T-BD | C4H9O2-E | $\sim O(CH_2)_4OH$ | 1,4 Butane diol end group |
| B-BD | C4H8O2-R | $\sim O(CH_2)_4O\sim$ | 1,4 Butane diol repeat unit |
| T-BUTENOL | C4H11O2-E | $\sim O(CH_2)_2CH{=}CH_2$ | Butenol end group |
| THF | C4H8O-4 |  | Tetrahydrofurane |

## *Table 4.11 Step-Growth Reactions for Terephthalate Polyesters*

| Reaction Type | Stoichiometric Reactions - Direct Esterification Route† |
|---|---|
| Condensation |  |
| Polymerization |  |
| Rearrangement |  |

| Reaction Type | Additional Reactions - Transesterification Route |
|---|---|
| Condensation |  |
| Polymerization |  |
| End-group Exchange |  |

*† x = 2 for polyethylene-terephthalate*

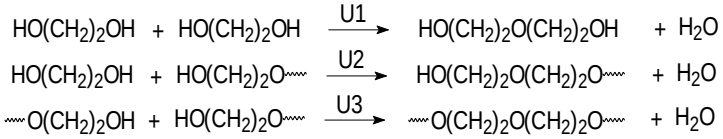
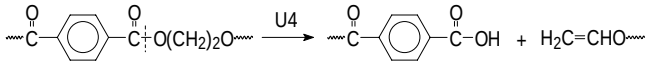
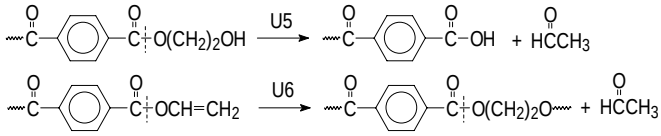
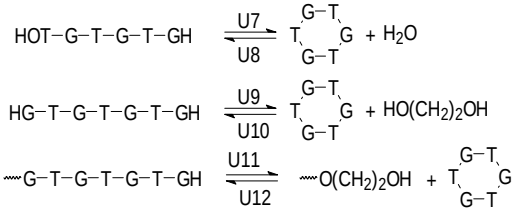
*x = 3 for polypropylene-terephthalate*

*x = 4 for polybutylene-terephthalate*

### *Table 4.12 Reaction Identifiers for PET Step-Growth Reactions*

| Reaction # | Attacking Nucleophilic Species | Victim Electrophilic Species | Victim Nucleophilic Species |
|---|---|---|---|
| 1 | EG | TPA | none |
| 2 | H2O | T-TPA | T-EG |
| 3 | T-EG | TPA | none |
| 4 | H2O | T-TPA | B-EG |
| 5 | EG | T-TPA | none |
| 6 | H2O | B-TPA | T-EG |
| 7 | T-EG | T-TPA | none |
| 8 | H2O | B-TPA | B-EG |
| 9 | T-EG | T-TPA | T-EG |
| 10 | EG | T-TPA | B-EG |
| 11 | T-EG | B-TPA | T-EG |
| 12 | EG | B-TPA | B-EG |
| 13 | T-EG | B-TPA | B-EG |
| 14 | T-EG | B-TPA | B-EG |
| 15 | EG | DMT | none |
| 16 | MEOH | T-DMT | T-EG |
| 17 | T-EG | DMT | none |
| 18 | MEOH | T-DMT | B-EG |
| 19 | EG | T-DMT | none |
| 20 | MEOH | B-TPA | T-EG |
| 21 | T-EG | T-DMT | none |
| 22 | MEOH | B-TPA | B-EG |
| 23 | T-EG | T-DMT | T-EG |
| 24 | EG | T-DMT | B-EG |
| 25 | H2O | T-DMT | none |
| 26 | MEOH | T-TPA | none |

## *Table 4.13 Side Reactions - Polyethylene Terephthalate Process*

| Reaction Type | Reaction Stoichiometry |
|---|---|
| DEG Formation |  |
| Thermal Scission |  |
| Acetaldehyde Formation |  |
| Cyclic Trimer Formation |  |

### *Table 4.14 Power-Law Exponents for User-Specified Reactions; Polyethylene Terephthalate Process*

| Reaction # | Power-Law Exponents; Modeling Notes |
|---|---|
| U1 | EG = 2 (Multiply group-based pre-exponential factor by 4.0) |
| U2 | EG = 1, T-EG = 1 (Multiply group-based pre-exponential factor by 2.0) |
| U3 | T-EG = 2 (Multiply group-based pre-exponential factor by 1.0) |
| U4 | Reaction is first order with respect to polyester repeat units, assume concentration of repeat units is approximately equal to the concentration of B-TPA, set power-law exponents B-TPA = 1.0 B-EG = 1x10-8 |
| U5 | T-EG = 1 |
| U6 | T-EG = 1, T-VINYL = 1 |
| U7 | Reaction is first order with respect to linear molecule with the following segment sequence:<br>T-TPA: B-EG : B-TPA : B-EG : B-TPA : T-EG<br>option 1: assume this concentration = TPA concentration and use power-law constant TPA = 1*<br>option 2: use the following equation, based on the most-probable distribution, to estimate the concentration of this linear oligomer. This equation can be implemented as a user-rate constant correlation<br>$[P_2] = \left(\frac{[T-EG]}{NUCL}\right)\left(\frac{[B-TPA]}{ELEC}\right)^2\left(\frac{[B-EG]}{NUCL}\right)^2\left(\frac{[T-TPA]}{ELEC}\right)\lambda_0$ $NUCL = [T-EG]+[T-DEG]+2*[B-EG]+2*[B-DEG]$ $ELEC = [T-TPA]+2*[B-TPA]$ |
| U8 | H2O = 1, C3 = 1 (Multiply group-based pre-exponential factor by 6.0) |
| U9 | Reaction is first order with respect to linear molecule with the following segment sequence:<br>T-EG : B-TPA : B-EG : B-TPA : B-EG : B-TPA : T-EG<br>option 1: assume this concentration = TPA concentration and use power-law constant TPA = 1*<br>option 2: use the following equation, based on the most-probable distribution, to estimate the concentration of this linear oligomer. This equation can be implemented as a user-rate constant correlation<br>$[P_2] = \left(\frac{[T-EG]}{NUCL}\right)^2\left(\frac{[B-TPA]}{ELEC}\right)^3\left(\frac{[B-EG]}{NUCL}\right)^2\lambda_0$ $NUCL = [T-EG]+[T-DEG]+2*[B-EG]+2*[B-DEG]$ $ELEC = [T-TPA]+2*[B-TPA]$ |
| U10 | EG = 1, C3 = 1 (Multiply group-based pre-exponential factor by 12.0) |
| U11 | Reaction is first order with respect to linear molecule with the following segment sequence:<br>~B-EG : B-TPA : B-EG : B-TPA : B-EG : B-TPA : T-EG<br>option 1: assume this concentration = T-EG concentration and use power-law constant T-EG = 1*<br>option 2: use the following equation, based on the most-probable distribution, to estimate the concentration of this linear oligomer. This equation can be implemented as a user-rate constant correlation<br>$[P_2] = \left(\frac{[T-EG]}{NUCL}\right)\left(\frac{[B-TPA]}{ELEC}\right)^3\left(\frac{[B-EG]}{NUCL}\right)^3\lambda_0$ $NUCL = [T-EG]+[T-DEG]+2*[B-EG]+2*[B-DEG]$ $ELEC = [T-TPA]+2*[B-TPA]$ |
| U12 | T-EG = 1, C3 = 1 (Multiply group-based pre-exponential factor by 6.0) |

* ***To avoid numerical problems, set power-law exponents to*** $1\times10^{-8}$ ***for reactants which do not appear in the rate expression***

$\lambda_0$ ***= concentration zeroth moment, mol/L***

***(approximately=0.5*([T-TPA]+[T-EG]+[T-DEG]+[T-VINYL])***

## Nylon-6 Reaction Kinetics

Nylon-6 melt-phase polymerization reactions are initialized by the hydrolytic scission of caprolactam rings. The reaction between water and caprolactam generates aminocaproic acid. The reaction kinetics in the primary reactor are sensitive to the initial water concentration.

The carboxylic and amine end groups of the aminocaproic acid molecules participate in condensation reactions, releasing water and forming polymer molecules. The resulting acid and amine end groups in the polymer react with each other and with aminocaproic acid, releasing more water.

The amine end of aminocaproic acid and amine ends in polymer react with caprolactam through ring addition. This reaction is the primary growth mechanism in the nylon-6 process.

*Cyclic Oligomers*

As the reactions proceed, intramolecular reactions involving linear polymer molecules generate cyclic oligomers. Cyclic oligomers ranging from the dimer through rings ten units long are reported in the literature. The concentration of each successive cyclic oligomer (dimer, trimer, etc.) falls off sharply, in accordance with the most probable distribution.

Reactions involving cyclic compounds are not considered in the reaction generation algorithm in the step-growth model. These reactions, including ring opening, ring closing, ring addition, and cyclodepolymerization, must be specified as user reactions.

Table 4.15 summarizes key components in the nylon-6 process. The component names in this table are used in the successive tables.

*Major Reactions*

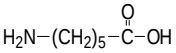
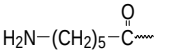
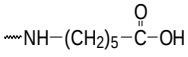
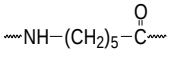
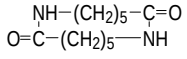
The major reactions in the nylon-6 process are shown in Table 4.16. Reactions 1-7 are considered in the reaction generation algorithm in the Step-Growth kinetics model. The rate constants for these reactions can be assigned according to the identifiers summarized in Table 4.17.

The reactions U1-U6, which involve cyclic monomer and dimer, are not generated by the current version of the Step-Growth model. These reactions must be defined as user reactions. The stoichiometry of each of these reactions is shown in Table 4.16. The suggested power-law exponents are shown in Table 4.18.

These side reactions are thought to be catalyzed by acid end groups in aminocaproic acid and the polymer. A first-order power-law coefficient can be used to account for the influence of the acid groups in these components. Alternately, a user rate-constant subroutine can be developed to account for the influence of the acid end groups.

Note that the forward and reverse terms of the reversible side reactions must be defined as two separate user reactions in the model.

## Table 4.15 Components to Simulate Nylon-6 Melt Polymerization

| Component ID | Databank ID | Component Structure | Component Name |
|---|---|---|---|
| CL | C6H11NO |  | ε-Caprolactam |
| ACA | none |  | Aminocaproic acid |
| T-NH2 | C6H12NO-E-1 |  | Amine end group segment |
| T-COOH | C6H12NO2-E-1 |  | Acid end group segment |
| R-NY6 | C6H11NO-R-1 |  | Nylon-6 repeat segment |
| CD | none |  | Cyclic dimer |
| H2O | H2O | $H_2O$ | Water |

## Table 4.16 Reactions in Nylon-6 Melt Polymerization Process

| Reaction Type | User-Specified Reactions (Forward and Reverse Reactions Defined Separately)† |
|---|---|
| Ring Opening / Ring Closing | U1 H2O + CL ⇌ ACA |
| | U2 H2O + CD ⇌ T-COOH : T-NH2 (=$P_2$) |
| Ring Addition / Cyclodepolymerization | U3 ACA + CL ⇌ T-COOH : T-NH2 (=$P_2$) |
| | U4 T-NH2 + CL ⇌ R-NY6 : T-NH2 |
| | U5 ACA + CD ⇌ T-COOH : R-NY6 : T-NH2 (=$P_3$) |
| | U6 T-NH2 + CD ⇌ R-NY6 : R-NY6 : T-NH2 |
| **Reaction Type** | **Model-Generated Step-Growth Reactions (Define Nylon-6 Repeat Unit as EN-GRP)** |
| Condensation | 1. ACA + ACA ⇌ T-COOH : T-NH2 + H2O |
| | 2. ACA + T-COOH ⇌ T-COOH : R-NY6 + H2O |
| | 3. T-NH2 + ACA ⇌ R-NY66 : T-NH2 + H2O |
| | 4. T-NH2 + T-COOH ⇌ R-NY66 : R-NY6 + H2O |
| Re-Arrangement | 5. T-NH2 + T-NH2 : T-COOH ⇌ T-NH2 : R-NY6 + ACA |
| | 6. T-NH2 + R-NY6 : T-COOH ⇌ R-NY6 : R-NY6 + ACA |
| | 7. T-NH2 + R-NY6 : R-NY6 ⇌ R-NY6 : R-NY6 + T-NH2 |

† ***In the reaction stoichiometry equations above, the colon (:) indicates connections between segments. Literature sources report re-arrangement reactions are insignificant, these reaction rates can be set to zero***

### *Table 4.17 Reaction Identifiers for Model-Generated Reactions; Nylon-6 Melt-Phase Polymerization Model*

| Reaction # | Attacking Nucleophilic Species | Victim Electrophilic Species | Victim Nucleophilic Species |
|---|---|---|---|
| 1 forward | ACA | T-ACA | none |
| 2 forward | ACA | T-COOH | none |
| 3 forward | T-NH2 | ACA | none |
| 4 forward | T-NH2 | T-COOH | none |
| 5 forward | T-NH2 | T-NH2 | T-COOH |
| 6 forward | T-NH2 | T-NH2 | R-NY6 |
| 7 forward | T-NH2 | R-NY6 | R-NY6 |
| 1 reverse | H2O | T-NH2 | T-COOH |
| 2 reverse | H2O | R-NY6 | T-COOH |
| 3 reverse | H2O | T-NH2 | R-NY6 |
| 4 reverse | H2O | R-NY6 | R-NY6 |
| 5 reverse | ACA | T-NH2 | R-NY6 |
| 6 reverse | ACA | R-NY6 | R-NY6 |
| 7 reverse | T-NH2 | R-NY6 | R-NY6 |

### *Table 4.18 Power-Law Exponents for User-Specified Reactions; Nylon-6 Melt Polymerization Model*

| Reaction # | Power-Law Exponents; Modeling Notes |
|---|---|
| U1 forward | H2O = 1, CL = 1 |
| U1 reverse | ACA = 1 |
| U2 forward | H2O = 1, CD = 1 (Multiply group-based pre-exponential factor by 2.0) |
| U2 reverse | Reaction is first order with respect to linear dimer $P_2$ with the following segment sequence:<br>T-NH2 :T-COOH<br>option 1: assume $P_2$ concentration = ACA concentration and use power-law constant ACA = 1*<br>option 2: use the following equation, based on the most-probable distribution, to estimate concentration of $P_2$ The denominator in this equation can be implemented as a user rate constant, with first-order power-law constants for T-NH2 and T-COOH.<br>$\left[P_2\right] = \left(\frac{[T-NH2]}{[T-NH2]+[R-NY6]}\right)\left(\frac{[T-COOH]}{[T-COOH]+[R-NY6]}\right)\lambda_0$ |
| U3 forward | ACA = 1, CL = 1 |
| U3 reverse | See U2 reverse reaction |
| U4 forward | T-NH2 = 1, CL = 1 |
| U4 reverse | T-NH2 = 1 (this approximation assumes most T-NH2 end groups are attached to repeat units)* |
| U5 forward | ACA = 1, CD = 1 |
| U5 reverse | Reaction is first order with respect to linear trimer $P_3$ with the following segment sequence:<br>T-NH2 : R-NY6 : T-COOH<br>option 1: assume $P_3$ concentration = ACA concentration and use power-law constant ACA = 1*<br>option 2: use the following equation, based on the most-probable distribution, to estimate concentration of $P_3$ The denominator in this equation can be implemented as a user rate constant, with first-order power-law constants for T-NH2, R-NY6, and T-COOH.<br>$\left[P_2\right] = \left(\frac{[T-NH2]}{[T-NH2]+[R-NY6]}\right)\left(\frac{[R-NY6]}{[T-COOH]+[R-NY6]}\right)\left(\frac{[T-COOH]}{[T-COOH]+[R-NY6]}\right)\lambda_0$ |
| U6 forward | T-NH2 = 1, CD = 1 |
| U6 reverse | T-NH2 = 1 (this approximation assumes most T-NH2 end groups are attached to repeat units)* |

* ***To avoid numerical problems, set power-law exponents to*** $1\times10^{-8}$ ***for reactants which do not appear in the rate expression***

$\lambda_0$ ***= concentration zeroth moment, mol/L (approximately = 0.5 * ([T-COOH] + [T-NH2])***

## Nylon-6,6 Reaction Kinetics

The salt process involves a preliminary reaction to form the salt, which precipitates from solution. During the salt formation, some of the salt remains in solution, leading to higher polymers. For a rigorous model, it is a good idea to consider these oligomerization reactions, even in the salt precipitation reactor. Accounting for these reactions is important when using the model to optimize the temperature, pressure, and water content of the nylon salt crystallizer.

The model needs to consider three phase equilibrium (solid salt, liquid, and vapor). Three phase equilibrium can be considered in Aspen Plus using the electrolyte chemistry feature. In version 10.0, however, the CSTR model does not allow a component to appear simultaneously in chemistry reactions and kinetic reactions. Another way to represent the solid-liquid equilibrium is to define an equilibrium reaction between the components representing the dissolved and solid salt. Chemical equilibrium equations can be defined using the Power-Law reaction kinetics model in Aspen Plus. Apply the “mole-gamma” option to force the equilibrium equation to use the ratio of the molar activities as the basis of the equilibrium constant. By using this assumption, the equilibrium constant is the same as the solubility constant of the solid salt.

To model the reaction kinetics of the salt process, the dissolved salt should be considered as a component in the reaction model. The models described in the open literature do this by considering the salt as an “AB” type monomer. This treatment, however, fails to consider some of the reverse reactions which can occur during polymerization. This approach assumes that reverse condensation reactions and re-arrangement reactions always generate products with an equal number of adipic acid and HMDA units. In reality, polymer chains with an unequal number of units can be formed because the reactions can occur inside the repeat units which originally came from the reacting salts. Further, the reverse reactions can generate free adipic acid or HMDA when the reaction occurs at the end of a polymer chain.

*Reverse Rate Constant*

The models in the literature use a reverse rate constant which is twice the reverse rate constant experienced by an individual amine group. This factor of two accounts for the fact that each repeat unit has two amine groups. In the approach described here, the reverse rate constants used in the model should be the rate constant between two functional groups, for example between water and a single amine group.

Considering salt as a component, there are several reversible reactions which must be considered in the model. A number of condensation reactions occur including those between molecules of dissolved salt, dissolved monomers, and polymer end groups. These reactions can be implemented in the step-growth model through the user reaction feature. The step-growth model will generate the reactions which do not involve the salt component.

The molecular weight distribution of nylon-6,6 is known to re-equilibrate when the polymer is exposed to HMDA under pressure. Further, as vacuum is applied, free HMDA appears to be generated. These facts indicate that rearrangement reactions are important in this process.

*Modeling Approaches*

Two modeling approaches are described in the Table 4.22 an d Table 4.23.. In the "simplified" approach, the dissolved salt is treated as an "AB" monomer (a monomer with two different types of functional groups). This is accomplished by defining the repeat unit as an "EN-GRP" reactive group. The simplified approach is consistent with the modeling approach described in the open literature.

The "detailed" modeling approach treats the HMDA and ADA segments as discreet molecular units. Using this assumption, the dissolved salt is a dimer made up of one hexamethylene diamine end group and one adipic acid end group. This approach is more rigorous because it considers every possible reverse reaction, including terminal monomer loss. To use this approach, define the HMDA repeat group as a bifunctional nucleophile (NN-GRP), and the ADA repeat group as a bifunctional electrophile (EE-GRP).

Table 4.19 shows the component definitions for both modeling approaches. The component names used in this table are used in the successive tables to document the reactions.

The reactions in the simplified model are shown in Table 4.20. Using this approach, the Step-Growth model will generate all of the main reactions. The solid-liquid phase equilibrium can be represented as a chemical equilibrium reaction using the Power-Law model or as two side reactions in the step-growth model. The equilibrium constant of this reaction corresponds to the solubility constant of the salt.

*Rate Constant Identifiers*

The rate constants can be assigned to these reactions using the identifiers summarized in Table 4.21. A subset of these identifiers can be used to assign the same rate constant to several different reactions. For example, reactions 3-7 can be lumped together by specifying "T-NH2" as the attacking nucleophilic species and by leaving the victim species identifiers blank (unspecified).

Table 4.22 shows the reactions in the detailed model. The solid-liquid phase equilibrium (reaction C1) is represented as previously described. The reactions involving the dissolved salt, U1-U6, must be defined as user reactions. Reactions 1-7, which do not involve the salt, are generated by the model automatically.

Rate constants can be assigned to reactions 1-7 using the identifiers summarized in Table 4.23. A subset of these identifiers can be used to assign the same rate constant to several different reactions. For example, reactions 3-7 can be lumped together by specifying "T-HMDA" as the attacking nucleophilic species and by leaving the victim species identifiers blank (unspecified).

Each reaction involving the dissolved salt must be defined as a user-reaction in the Step-Growth model. The forward and reverse reactions are treated as two separate reactions. The stoichiometry of each reaction is shown in Table 4.22. The power-law exponents are shown in Table 4.24.

Several of the reverse reactions require a particular sequence of segments in order to occur. The concentration of molecules with these particular sequences can be assumed (for example, assume the linear trimer concentration is the same as the dissolved salt concentration) or they can be estimated from statistical arguments. Table 4.24 shows both techniques. The statistical approach is more rigorous, but it requires writing a user rate-constant or user kinetic subroutine to perform the calculations as shown.

### *Table 4.19 Components to Simulate Nylon-6,6 Processes*

| Components Common to Simplified and Detailed Approach | | | |
|---|---|---|---|
| **Component ID** | **Databank ID** | **Component Structure** | **Component Name** |
| ADA | C6H10O4-D1 | $HO-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-OH$ | Adipic acid |
| HMDA | C6H16N2 | $H_2N-(CH_2)_6-NH_2$ | Hexamethylene diamine |
| DIS-SALT | none | $HO-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-NH-(CH_2)_6-NH_2$ | Dissolved nylon-6,6 salt |
| SOL-SALT | none | $HO-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-O^{-}\,{}^{+}H_3N-(CH_2)_6-NH_2$ | Solid nylon-6,6 salt |
| MEOH | CH4O | $CH_3OH$ | Methanol |
| H2O | H2O | $H_2O$ | Water |
| **Segments In Simplified Salt Process Model** | | | |
| T-COOH | none | $HO-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-NH-(CH_2)_6-NH\sim$ | Acid end group segment |
| T-NH2 | none | $\sim\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-NH-(CH_2)_6-NH_2$ | Amine end group segment |
| R-NY66 | none | $\sim\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-NH-(CH_2)_6-NH\sim$ | Repeat unit segment |
| **Segments In Detailed Salt Process Model and Melt-Process Model** | | | |
| T-ADA | C6H9O3-E | $\sim\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-OH$ | Adipic acid end group |
| B-ADA | C6H8O2-R | $\sim\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}\sim$ | Adipic acid repeat unit |
| T-HMDA | C6H15N2-E | $\sim HN-(CH_2)_6-NH_2$ | HMDA end group |
| B-HMDA | C6H14N2-R | $\sim HN-(CH_2)_6-NH\sim$ | HMDA repeat unit |

### *Table 4.20 Reactions in Nylon-6,6 Salt Process; Simplified Model*

| **Reaction Type** | **Phase Equilibrium Reactions (Use Power-Law Reaction Kinetics Model)** |
|---|---|
| Solid/Liquid Equilibrium | C1 DIS-SALT + H2O ⇌ SOL-SALT |
| **Reaction Type** | **User-Specified Reactions (Forward and Reverse Reactions Defined Separately)** |
| Salt formation | U1 HMDA + ADA ⇌ DIS-SALT + H2O |
| **Reaction Type** | **Model-Generated Step-Growth Reactions (Define Nylon-6,6 Repeat Unit as EN-GRP)†** |
| Condensation | 1. DIS-SALT + DIS-SALT ⇌ T-COOH : T-NH2 + H2O |
| | 2. DIS-SALT + T-COOH ⇌ T-COOH : R-NY66 + H2O |
| | 3. T-NH2 + DIS-SALT ⇌ R-NY66 : T-NH2 + H2O |
| | 4. T-NH2 + T-COOH ⇌ R-NY66 : T-NY66 + H2O |
| Re-Arrangement | 5. T-NH2 + T-COOH : T-NH2 ⇌ R-NY66 : T-NH2 + DIS-SALT |
| | 6. T-NH2 + T-COOH : R-NY66 ⇌ R-NY66 : R-NY66 + DIS-SALT |
| | 7. T-NH2 + R-NY66 : R-NY66 ⇌ R-NY66 : R-NY66 + T-NH2 |

† ***In the reaction stoichiometry equations above, the colon (:) indicates connections between segments***

### *Table 4.21 Reaction Identifiers for Model-Generated Reactions; Simplified Nylon-6,6 Salt-Process Model*

| Reaction # | Attacking Nucleophilic Species | Victim Electrophilic Species | Victim Nucleophilic Species |
|---|---|---|---|
| 1 forward | DIS-SALT | DIS-SALT | none |
| 2 forward | DIS-SALT | T-COOH | none |
| 3 forward | T-NH2 | DIS-SALT | none |
| 4 forward | T-NH2 | T-COOH | none |
| 5 forward | T-NH2 | T-COOH | T-NH2 |
| 6 forward | T-NH2 | T-COOH | R-NY66 |
| 7 forward | T-NH2 | R-NY66 | R-NY66 |
| 1 reverse | H2O | T-COOH | T-NH2 |
| 2 reverse | H2O | T-COOH | R-NY66 |
| 3 reverse | H2O | R-NY66 | T-NH2 |
| 4 reverse | H2O | R-NY66 | R-NY66 |
| 5 reverse | DIS-SALT | T-NH2 | R-NY66 |
| 6 reverse | DIS-SALT | R-NY66 | R-NY66 |
| 7 reverse | T-NH2 | R-NY66 | R-NY66 |

### *Table 4.22 Reactions in Nylon-6,6 Salt Process - Detailed Model*

| Reaction Type | Phase Equilibrium Reactions (Use Power-Law Reaction Kinetics Model) |
|---|---|
| Solid/Liquid Equilibrium | C1 DIS-SALT + H2O ⇌ SOL-SALT |
| **Reaction Type** | **User-Specified Reactions (Forward and Reverse Reactions Defined Separately)†** |
| Salt formation | U1 HMDA + ADA ⇌ DIS-SALT + H2O |
| Condensation | U2 DIS-SALT + DIS-SALT ⇌ T-HMDA : B-ADA : B-HMDA : T-ADA + H2O |
| | U3 DIS-SALT + ADA ⇌ T-ADA : B-HMDA : T-ADA + H2O |
| | U4 HMDA + DIS-SALT ⇌ T-HMDA : B-ADA : T-HMDA + H2O |
| | U5 DIS-SALT + T-ADA ⇌ T-ADA : B:HMDA : B-ADA + H2O |
| | U6 T-HMDA + DIS-SALT ⇌ B-HMDA : B-ADA : T-HMDA + H2O |
| **Reaction Type** | **Model-Generated Step-Growth Reactions (Define B-HMDA as NN-GRP, B-ADA as EE-GRP)** |
| Condensation | 1. HMDA + ADA ⇌ T-HMDA : T-ADA + H2O |
| | 2. HMDA + T-ADA ⇌ T-HMDA : B-ADA + H2O |
| | 3. T-HMDA + ADA ⇌ B-HMDA : B-ADA + H2O |
| | 4. T-HMDA + T-ADA ⇌ B-HMDA + B-ADA + H2O |
| Re-Arrangement | 5. T-HMDA + T-ADA : T-HMDA ⇌ T-ADA : B-HMDA + HMDA |
| | 6. T-HMDA + B-ADA : T-HMDA ⇌ B-ADA : B-HMDA + HMDA |
| | 7. T-HMDA + B-ADA : B-HMDA ⇌ B-ADA : B-HMDA + T-HMDA |

† ***In the reaction stoichiometry equations above, the colon (:) indicates connections between segments***

### *Table 4.23 Reaction Identifiers for Model-Generated Reactions; Detailed Nylon-6,6 Salt-Process Model and Melt-Phase Model*

| Reaction # | Attacking Nucleophilic Species | Victim Electrophilic Species | Victim Nucleophilic Species |
|---|---|---|---|
| 1 forward | HMDA | ADA | none |
| 2 forward | HMDA | T-ADA | none |
| 3 forward | T-HMDA | ADA | none |
| 4 forward | T-HMDA | T-ADA | none |
| 5 forward | T-HMDA | T-ADA | T-HMDA |
| 6 forward | T-HMDA | B-ADA | T-HMDA |
| 7 forward | T-HMDA | B-ADA | B-HMDA |
| 1 reverse | H2O | T-ADA | T-HMDA |
| 2 reverse | H2O | B-ADA | T-HMDA |
| 3 reverse | H2O | T-ADA | B-HMDA |
| 4 reverse | H2O | B-ADA | B-HMDA |
| 5 reverse | HMDA | T-ADA | B-HMDA |
| 6 reverse | HMDA | B-ADA | B-HMDA |
| 7 reverse | T-HMDA | B-ADA | B-HMDA |

### *Table 4.24 Power-Law Exponents for User-Specified Reactions; Detailed Nylon-6,6 Salt-Process Model*

| Reaction # | Power-Law Exponents; Modeling Notes |
|---|---|
| U1 forward | HMDA = 1, ADA = 1 Multiply group-based pre-exponential factor by 4.0 |
| U1 reverse | H2O = 1, DIS-SALT = 1 |
| U2 forward | DIS-SALT = 2 |
| U2 reverse | Reaction is first order with respect to water and polymer molecule $P_4$ with the following segment sequence:<br>T-HMDA : B-ADA : B-HMDA : T-ADA<br>option 1: assume $P_4$ concentration = DIS-SALT concentration and use DIS-SALT = 1, H2O = 1<br>option 2: set power-law exponent for H2O = 1 and use the following equation, based on the most-probable distribution, to estimate concentration of $P_4$ (this equation can be implemented as a user rate constant).<br>$$[P_4] = \left(\frac{[T-ADA]}{[T-ADA]+2[B-ADA]}\right)\left(\frac{2[B-HMDA]}{[T-HMDA]+2[B-HMDA]}\right)$$<br>$$\left(\frac{2[B-ADA]}{[T-ADA]+2[B-ADA]}\right)\left(\frac{[T-HMDA]}{[T-HMDA]+2[B-HMDA]}\right)\lambda_0$$ |

* ***To avoid numerical problems, set power-law exponents to*** $1\times10^{-8}$ ***for reactants which do not appear in the rate expression***

$\lambda_0$ ***= concentration zeroth moment, mol/L (approximately = 0.5 * ([T-ADA] + [T-HMDA])***

*continued*

## *Table 4.24 Power-Law Exponents for User-Specified Reactions; Detailed Nylon-6,6 Salt-Process Model (cont.)*

| Reaction # | Power-Law Exponents; Modeling Notes |
|---|---|
| U3 forward | DIS-SALT = 1, ADA = 1, multiply group rate constant by 2.0 |
| U3 reverse | Reaction is first order with respect to water and polymer molecule $P_{3,aa}$ with the following segment sequence:<br>T-ADA : B-HMDA : T-ADA<br>option 1: assume $P_{3,aa}$ concentration = ADA concentration and use power-law constants ADA = 1, H2O = 1<br>option 2: set power-law exponent for H2O = 1 and use the following equation, based on the most-probable distribution, to estimate concentration of $P_{3,aa}$ (this equation can be implemented as a user rate constant).<br>$\left[P_{3,aa}\right] = \left(\frac{[T-ADA]}{[T-ADA]+2[B-ADA]}\right)^2 \left(\frac{2[B-HMDA]}{[T-HMDA]+2[B-HMDA]}\right) \lambda_0$ |
| U4 forward | DIS-SALT = 1, HMDA = 1; multiply group rate constant by 2.0 |
| U4 reverse | Reaction is first order with respect to water and polymer molecule $P_{3,BB}$ with the following segment sequence:<br>T-HMDA : B-ADA : T-HMDA<br>option 1: assume $P_{3,BB}$ concentration=HMDA concentration and use power-law constants HMDA=1, H2O=1<br>option 2: set power-law exponent for H2O = 1 and use the following equation, based on the most-probable distribution, to estimate concentration of $P_{3,BB}$ (this equation can be implemented as a user rate constant).<br>$\left[P_{3,aa}\right] = \left(\frac{[T-HMDA]}{[T-HMDA]+2[B-HMDA]}\right)^2 \left(\frac{2[B-ADA]}{[T-ADA]+2[B-ADA]}\right) \lambda_0$ |
| U5 forward | DIS-SALT = 1, T-ADA = 1 |
| U5 reverse | H2O = 1, T-ADA = 1, set power law constants for B-ADA, B-HMDA to 1E-10 to avoid numerical problems |
| U6 forward | DIS-SALT = 1, T-HMDA = 1 |
| U6 reverse | H2O = 1, T-ADA = 1, set power law constants for B-ADA, B-HMDA to 1E-10 to avoid numerical problems |

* ***To avoid numerical problems, set power-law exponents to*** $1\times10^{-8}$ ***for reactants which do not appear in the rate expression***

$\lambda_0$ ***= concentration zeroth moment, mol/L (approximately = 0.5 * ([T-ADA] + [T-HMDA])***

## Melt-Phase Polymerization

The best way to model the melt-phase polymerization of nylon-6,6 is to treat the HMDA and ADA segments as discreet molecular as shown in Table 4.19.

Table 4.25 shows the main reactions in the melt-phase polymerization of nylon-6,6. These reactions are generated by the Step-Growth model if the HMDA repeat group is defined as a bifunctional nucleophile (NN-GRP), and the ADA repeat group as a bifunctional electrophile (EE-GRP).

Side reactions which are not shown in Table 4.25 may be included in the model as "user reactions".

Rate constants can be assigned to reactions 1-7 using the identifiers summarized in Table 4.23. A subset of these identifiers can be used to assign the same rate constant to several different reactions. For example, reactions 3-7 can be lumped together by specifying "T-HMDA" as the attacking nucleophilic species and by leaving the victim species identifiers blank (unspecified).

### *Table 4.25 Reactions in Nylon-6,6 Melt Process*

| Reaction Type | Model-Generated Step-Growth Reactions (Define B-HMDA as NN-GRP, B-ADA as EE-GRP)† |
|---|---|
| Condensation | 1. HMDA + ADA $\rightleftharpoons$ T-HMDA : T-ADA + H2O |
| | 2. HMDA + T-ADA $\rightleftharpoons$ T-HMDA : B-ADA + H2O |
| | 3. T-HMDA + ADA $\rightleftharpoons$ B-HMDA : B-ADA + H2O |
| | 4. T-HMDA + T-ADA $\rightleftharpoons$ B-HMDA + B-ADA + H2O |
| Re-Arrangement | 5. T-HMDA + T-ADA : T-HMDA $\rightleftharpoons$ T-ADA : B-HMDA + HMDA |
| | 6. T-HMDA + B-ADA : T-HMDA $\rightleftharpoons$ B-ADA : B-HMDA + HMDA |
| | 7. T-HMDA + B-ADA : B-HMDA $\rightleftharpoons$ B-ADA : B-HMDA + T-HMDA |

† ***In the reaction stoichiometry equations above, the colon (:) indicates connections between segments***

## Melt Polycarbonate Reaction Kinetics

There is little information regarding melt-phase polymerization of polycarbonate available in the public domain. From what is available, it is clear that the chemistry of the melt-polycarbonate process follows the typical pattern for step-growth condensation involving two dissimilar monomers. The bisphenol-A monomer behaves as a bifunctional nucleophile, and the diphenyl carbonate monomer behaves as a bifunctional electrophile. The reactions generate phenol as a by-product. In later stages of the process, rearrangement reactions regenerate small amounts of bisphenol-A monomer.

Table 4.26 summarizes the most convenient method for characterizing the components involved in the melt polycarbonate process.

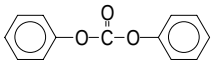
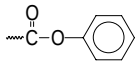
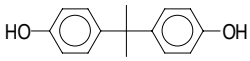
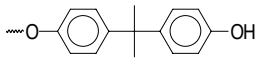
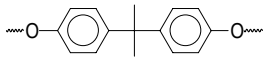
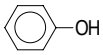
Table 4.27 shows the main reactions in this process. These reactions are generated by the model if the carbonate group is defined as a bifunctional electrophile (EE-GRP) and the BPA group as a bifunctional nucleophile (NN-GRP).

Table 4.28 shows how to assign rate constants to each of the reactions shown in Table 4.27. Rate constants can be assigned to several by leaving some of the reaction identifiers unspecified. For example, the reverse reactions involving phenol can be lumped together by assigning phenol as the attacking nucleophilic species and by leaving the names of the victim species unspecified.

The open literature does not describe the side reactions involved in this process, although side reactions are certainly known to exist. These side reactions can be added to the model as “user reactions”.

## Table 4.26 Components to Simulate Melt Polycarbonate Processes

**Components Common to Simplified and Detailed Approach**

| Component ID | Databank ID | Component Structure | Component Name |
|---|---|---|---|
| DPC | none |  | Diphenyl Carbonate |
| T-DPC | C7H5O2-E |  | Phenyl carbonate end group |
| B-DPC | CO-R |  | Carbonate repeat unit |
| BPA | C15H16O2 |  | Bisphenol-A |
| T-BPA | C15H15O2-E |  | Bisphenol-A end group |
| B-BPA | C15H14O2-R |  | Bisphenol-A repeat unit |
| PHOH | C6H6O |  | Phenol |

## Table 4.27 Reactions in the Melt Polycarbonate Process

| Reaction Type | Model-Generated Step-Growth Reactions (Define B-BPA as NN-GRP, B-DPC as EE-GRP)† |
|---|---|
| Condensation | 1. BPA + DPC ⇌ T-BPA : T-DPC + PHOH |
| | 2. BPA + T-DPC ⇌ T-BPA : B-DPC + PHOH |
| | 3. T-BPA + DPC ⇌ B-BPA : B-DPC + PHOH |
| | 4. T-BPA + T-DPC ⇌ B-BPA + B-DPC + PHOH |
| Re-Arrangement | 5. T-BPA + T-DPC : T-BPA ⇌ T-DPC : B-BPA + BPA |
| | 6. T-BPA + B-DPC : T-BPA ⇌ B-DPC : B-BPA + BPA |
| | 7. T-BPA + B-DPC : B-BPA ⇌ B-DPC : B-BPA + T-BPA |

† ***In the reaction stoichiometry equations above, the colon (:) indicates connections between segments***

### *Table 4.28 Reaction Identifiers for Model-Generated Reactions; Melt Polycarbonate Process*

| Reaction # | Attacking Nucleophilic Species | Victim Electrophilic Species | Victim Nucleophilic Species |
|---|---|---|---|
| 1 forward | BPA | DPC | none |
| 2 forward | BPA | T-DPC | none |
| 3 forward | T-BPA | DPC | none |
| 4 forward | T-BPA | T-DPC | none |
| 5 forward | T-BPA | T-DPC | T-BPA |
| 6 forward | T-BPA | B-DPC | T-BPA |
| 7 forward | T-BPA | B-DPC | B-BPA |
| 1 reverse | PHOH | T-DPC | T-BPA |
| 2 reverse | PHOH | B-DPC | T-BPA |
| 3 reverse | PHOH | T-DPC | B-BPA |
| 4 reverse | PHOH | B-DPC | B-BPA |
| 5 reverse | BPA | T-DPC | B-BPA |
| 6 reverse | BPA | B-DPC | B-BPA |
| 7 reverse | T-BPA | B-DPC | B-BPA |

# MODEL FEATURES AND ASSUMPTIONS

## Model Predictions

The step-growth model calculates the component reaction rates and the rate of change of the zeroth and first polymer moments $(\lambda_0, \lambda_1^i)$ of the polymer chain length distribution. The number average polymer properties (Pn, Mn) are calculated from the moments. These component attributes can be used to calculate secondary properties, such as polymer viscosity, melting point, end group concentrations, intrinsic viscosity, melt flow index, etc. Correlations relating secondary properties to the polymer moments can be implemented using a User Prop-Set Property subroutine, as described in the *Aspen Plus User Manuals*.

## Phase Equilibria

The model assumes that all reactions occur in the liquid phase. Single-phase (L), two-phase (VL) and three-phase (VLS) systems are within the scope of the model. This restricts the general model to melt-phase, solution, and bulk polymerization processes.

Interfacial polymerization involves a solvent phase, an organic monomer phase, and a polymer phase. The reaction rate is usually limited by the rate of mass transfer of monomers from the organic phase to the reacting polymer phase. This physical situation is not considered in any of the standard reactor models in Polymers Plus. These systems can be simulated by developing a custom reactor model in Aspen Custom Modeler or Aspen Plus, or by writing an appropriate concentration basis subroutine for the step-growth model.

Solid-state polymerization involves crystalline and amorphous solid polymer phases and a vapor phase. The reaction kinetics may be limited by the rate of mass transfer of volatile reaction by-products from the amorphous solid phase to the polymer phase. None of the standard reactor models in Polymers Plus are designed for solid-state polymerization. Solid-state polymerization models can be developed in Aspen Custom Modeler and interfaced to the step-growth polymerization model through the Aspen Custom Modeler / Polymers Plus Interface.

Mass transfer limitations in thin-film or horizontal finishing reactors can be considered by customizing the Step-Growth model using the available concentration basis subroutine or by developing an appropriate user reactor model in Aspen Plus or Aspen Custom Modeler.

## Reaction Mechanism

The Step-Growth reaction model applies to condensation polymerization. In the future the model will be extended to cover pseudocondensation and ring-addition polymerization. The model accounts for any combination of monofunctional and bifunctional monomers. Cyclic monomers and multifunctional monomers, however, are not included in the standard reaction scheme.

User-defined stoichiometric reactions can be added to the model to account for reactions which are not included in the standard reaction scheme. These reactions use a power-law rate expression which can be extended to more complex rate expressions through the application of a user-written Fortran subroutine.

# MODEL STRUCTURE

This section outlines the structure of the Step-Growth kinetics model. It examines the theoretical framework in detail. The assumptions and limits of the algorithms are documented.

## Reacting Groups and Species

The first step in the development of any process simulation model is to determine the list of components. In Polymers Plus it is also important to decide how to characterize the polymer components. A polymer can be broken down into segments any number of ways. For example, the nylon-6 repeat unit can be treated as a segment, or it can be divided into two segments corresponding to the portions of the repeat unit which came from the diacid and diamine monomers.

### Segments

The preferred method of segmenting the polymer component is to define segments corresponding to the monomers which are used to produce the polymer. This technique has two distinct advantages. First, the property models in Polymers Plus use the monomer as a reference point for molecular size. Second, the reaction kinetics usually involve adding monomers to the end of growing polymer chains. Defining segments corresponding to the monomers makes it easy to write reactions corresponding to monomers and segments, for example monomer “A” $\rightarrow$ segment “A”.

The Step-Growth model assumes that the polymer is segmented in this manner. For monadic polymers such as nylon-6, this technique is straightforward. This method of segmenting the polymer is a bit unusual for dyadic polymers, such as PET, because it treats them as alternating copolymers. Thus, a molecule of PET with 100 PET units is defined as having a degree of polymerization of 200 in this model (100 terephthalate units and 100 glycol units).

Monofunctional monomers, such as benzoic acid, always correspond to an end-group segment in the model. Bifunctional monomers can end up inside a linear polymer chain as a repeat unit, or may be located at the end of the chain as an end group. Each symmetric bifunctional monomer (diacids, diols, diamines, etc.) corresponds to one repeat segment and one end-group segment. Asymmetric bifunctional monomers (monomers with two different types of end groups) correspond to one repeat unit and two end-group segments. Multifunctional monomers can correspond to several segments, as shown in Table 4.29.

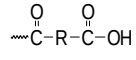
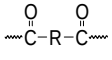
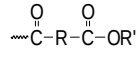
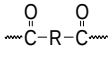
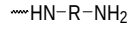
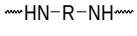
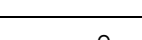
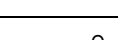
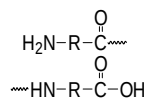
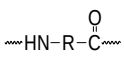
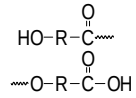
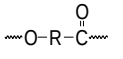
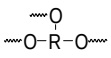
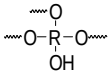
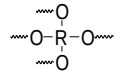
## Reacting Functional Groups

The Step-Growth reaction model generates reactions based on the types of functional groups found in the reactants. The model includes a list of pre-defined group types, as shown in Table 4.30.

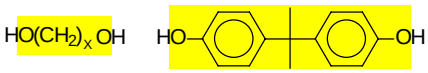
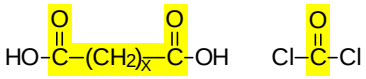
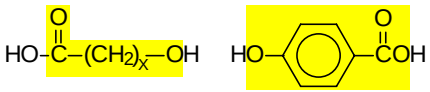
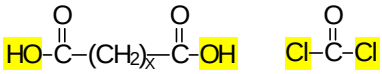
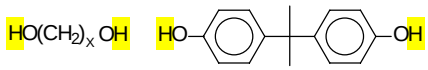
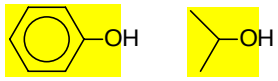
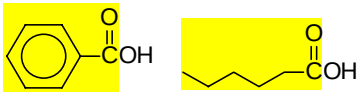
Each functional group in the model is assigned a name and type. The names are used to distinguish between different groups with the same chemical functionality.

Table 4.31 shows the types of functional groups found in common monomers and the condensate products.

## *Table 4.29 Segments Corresponding to Common Types of Monomers*

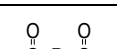
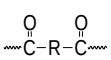
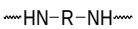
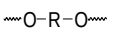
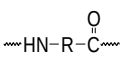
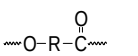
| Monomer Type | Monomer Formula | Corresponding Segment Formulas | | | |
|---|---|---|---|---|---|
| | | End-Groups | Repeat Unit | Branch-3 | Branch-4 |
| Acid |  |  | --- | --- | --- |
| Ester |  |  | --- | --- | --- |
| Amine |  |  | --- | --- | --- |
| Alcohol |  |  | --- | --- | --- |
| Diacid |  |  |  | --- | --- |
| Diester |  |  |  | --- | --- |
| Carbonate |  |  |  | --- | --- |
| Diamine |  |  |  | --- | --- |
| Diol |  |  |  | --- | --- |
| Amino acid |  |  |  | --- | --- |
| Lactic acid |  |  |  | --- | --- |
| Branch agent | $R(OH)_3$ | ~O-R(OH)$_2$ | ~O-R(OH)O~ |  | --- |
| Branch agent | $R(OH)_4$ | ~O-R(OH)$_3$ | ~O-R(OH)$_2$O~ |  |  |

## *Table 4.30 Reacting Functional Group Types*

| Description | Type | Examples† |
|---|---|---|
| Nucleophilic repeat units have two electron-strong sites. | NN-GRP |  |
| Electrophilic repeat units have two electron-weak sites. | EE-GRP |  |
| Mixed repeat units have one electrophilic site and one nucleophilic site. | EN-GRP |  |
| Nucleophilic leaving groups are electron-strong end groups. | N-GRP |  |
| Electrophilic leaving groups are electron-weak end groups. | E-GRP |  |
| Nucleophilic modifiers are groups with a single nucleophilic site. | NX-GRP |  |
| Electrophilic modifiers are groups with a single electrophilic site. | EX-GRP |  |

*† Highlighted portion of component is the named reacting functional group.*

### *Table 4.31 Reacting Functional Groups In Common Types of Monomers*

| Monomer Type | Monomer Formula | Reacting Functional Groups | | | | | |
|---|---|---|---|---|---|---|---|
| | | Leaving Groups | | | | Segment Groups | |
| | | Structure | Type | Structure | Type | Structure | Type |
| Acid |  | ~OH | N-GRP | --- | --- |  | EX-GRP |
| Ester |  | ~OR' | N-GRP | --- | --- |  | EX-GRP |
| Amine |  | ~H | E-GRP | --- | --- |  | NX-GRP |
| Alcohol |  | ~H | E-GRP | --- | --- |  | NX-GRP |
| Diacid |  | ~OH | N-GRP | --- | --- |  | EE-GRP |
| Diester |  | ~OR' | N-GRP | --- | --- |  | EE-GRP |
| Carbonate |  | ~OR | N-GRP | --- | --- |  | EE-GRP |
| Diamine |  | ~H | E-GRP | --- | --- |  | NN-GRP |
| Diol |  | ~H | E-GRP | --- | --- |  | NN-GRP |
| Amino acid |  | ~H (amine) | E-GRP | ~OH (acid) | N-GRP |  | EN-GRP |
| Lactic acid |  | ~H (alcohol) | E-GRP | ~OH (acid) | N-GRP |  | EN-GRP |
| **Reacting Functional Groups In Common Types of Condensate Products** | | | | | | | |
| Water |  | ~H | E-GRP | ~OH | N-GRP | | |
| Alcohol | RO-H | ~H | E-GRP | ~OR | N-GRP | | |

## Reacting Species

Since polymer components do not have a fixed structure, polymerization reactions must be written in terms of the polymer segments. The segments and standard components that make up the step-growth reaction network are referred to as reacting species. Each of these reacting species is made up of one or more reacting functional groups.

Once the reacting groups are defined, the structure of each reacting species is specified by defining the number of each reacting group in each reacting species. It is not necessary to specify a zero when a particular group is not in the species being defined.

*Species Structure Validity*

The model checks the species structures to verify they are valid and to see if there are any missing species. Species structures are considered valid if they follow these rules:

1. Species may not be oligomer or polymer components.
2. Species may include one EE-GRP, NN-GRP, or EN-GRP, but no species may have more than one of these three group types. Species may not contain more than one of any of these three groups.
3. Species which are end group segments must include one E-GRP or one N-GRP.
4. Species which are repeat segments may not include an E-GRP or N-GRP.
5. Species which are monomers must have a balanced number of electrophilic groups and nucleophilic groups.
6. Structures are unique - no two species may have the same structure.

The model determines every valid combination of the specified functional groups. Any combination which is not represented by a species structure is assumed to be a missing component. The model reports a warning message describing the structure of the species which was not specified and drops all reactions which would have involved this component. You can choose to ignore this warning if the missing component is unimportant in the process being simulated.

## Oligomer Fractionation

You can choose to include one or more oligomer components in the model. When this feature is used, the model will fractionate the polymer distribution between the polymer component and the various oligomer components. The fractionation algorithm assumes that the polymer follows the most probable distribution. These assumptions are valid when the reactions are reversible and when the rate of rearrangement reactions is faster than the rate of the condensation reactions. The logic of the fractionation algorithm is summarized in Table 4.32.

The oligomer feature can be used to track the loss of volatile short-chain oligomers from the polymer solution or melt. It can also be used to estimate oligomer concentrations to calculate reaction rates for ring closing reactions or other reactions which require a particular sequence of segments. Tracking oligomers, however, does require more simulation time and may make the model more difficult to converge.

## Table 4.32 Summary of Step-Growth Oligomer Fractionation Algorithm

**Assumptions**

- Polymer molecules consist of alternating nucleophilic and electrophilic segments
- Repeat segments in AB polymers, which are made up of EN-GRP groups, act as both a nucleophile and an electrophile. The end groups act as either electrophilic or nucleophilic segments, depending on which leaving group is attached to the end.
- The probability of a particular segment being in a given point in the segment sequence is determined by the concentration of that segment and the concentration of all other segments of that type (note: this assumption is equivalent to assuming the most-probable distribution).

**Equation**

Definition of probability factors used to determine probability of a given sequence of segments:

$$P_a = \frac{f_a N_a}{\sum_i f_i N_i} \qquad P_b = \frac{f_b E_b}{\sum_j f_j E_j}$$

$P_a$ = probability that nucleophilic segment a occupies the next nucleophilic position in the chain

$P_b$ = probability that electrophilic segment b occupies the next electrophilic position in the chain

$f_a$ = number of similar points of attachment in nucleophilic segment a (= 2 for repeat segments which are composed of an NN-GRP)

$f_b$ = number of similar points of attachment in electrophilic segment b (= 2 for repeat segments which are composed of an EE-GRP)

$N_a$ = concentration of nucleophilic segment “a”

$E_b$ = concentration of electrophilic segment “b”

$i$ = index corresponding to list of all nucleophilic segments

$j$ = index corresponding to list of all electrophilic segments

Example 1: calculation of expected concentration of oligomer with a sequence “ab”

$$C_{ab} = P_a P_b \lambda_0$$

$C_{ab}$ = expected oligomer concentration

$\lambda_0$ = concentration zeroth moment of polymer (concentration of all polymer molecules)

Example 2: calculation of expected concentration of oligomer with a sequence “aBABa”

$$C_{aBABa} = P_a^2 P_B^2 P_A \lambda_0$$

## Reaction Stoichiometry Generation

The model predicts the stoichiometry of each step-growth reaction based on the structure of each of the reactants. The reaction generation algorithm is summarized in Table 4.33.

***Table 4.33 Summary of Step-Growth Reaction Generation Algorithm***

| Reaction Type | Reaction Scheme | Reaction Generation Algorithm |
|---|---|---|
| Condensation - Monomer Addition | $M_{xa} + M_{yb} \rightarrow P_{2,xy} + W_{ab}$<br>$P_{n,xa} + M_{yb} \rightarrow P_{n+1,xy} + W_{ab}$<br>$M_{xa} + P_{n,yb} \rightarrow P_{n+1,yx} + W_{ab}$ | Find every combination by which nucleophilic monomers, $M_{xa}$, or end segments $P_{xa}$, can react with electrophilic monomers, $M_{yb}$, or end segments, $P_{yb}$, to give a condensate molecule, $W_{ab}$ |
| Condensation - Polymer Addition | $P_{n,xa} + P_{m,yb} \rightarrow P_{n+m,xy} + W_{ab}$ | Find every combination by which nucleophilic end segments, $P_{xa}$, can react with end segments, , $P_{yb}$, to give a condensate molecule, $W_{ab}$ |
| Reverse Condensation - Terminal Monomer Loss | $W_{ab} + P_{2,xy} \rightarrow M_{xa} + M_{yb}$<br>$W_{ab} + P_{n,xy} \rightarrow P_{n-1,xa} + M_{yb}$ | Find every combination by which a condensate molecule, $W_{ab}$, can react with a polymer molecule at the boundary between a nucleophilic repeat segment, x, and an electrophilic end group segment, y |
| Reverse Condensation - Scission | $W_{ab} + P_{n,xy} \rightarrow P_{n-m,xa} + P_{m,yb}$ | Find every combination by which a condensate molecule, $W_{ab}$, can react with a polymer molecule at the boundary between a nucleophilic repeat segment, x, and an electrophilic repeat segment, y |
| Forward Polycondensation | $P_{n,za} + P_{m,yx} \rightarrow P_{n+m-1,yz} + M_{xa}$ | Find every combination by which a nucleophilic end group segment. $P_{za}$, can react with a polymer molecule at the boundary between a nucleophilic repeat segment, x, and an electrophilic end segment, y |
| Reverse Polycondensation | $M_{za} + P_{n,yx} \rightarrow P_{n-m,yz} + P_{m+1,xa}$ | Find every combination by which a nucleophilic monomer, $M_{xa}$, can react with a polymer molecule at the boundary between a nucleophilic repeat segment, x, and an electrophilic end segment, y |
| Re-arrangement | $P_{n,za} + P_{m,xy} \rightarrow P_{n+m-q,yz} + P_{q,xa}$ | Find every combination by which a nucleophilic end group segment. $P_{za}$, can react with a polymer molecule at the boundary between a nucleophilic repeat segment, x, and an electrophilic repeat segment, y |

## Model-Generated Reactions

There are two steps required to assign rate constants to model generated reactions. First, the rate constant values are specified in the Step-Growth Rate Constant form (SG-RATE-CON sentence). Then each set of rate constants is assigned a number for identification. Once the rate constants sets are defined, they can be assigned to the generated reactions.

### Rate Expression for Model Generated Reactions

The Step-Growth reactions model uses a modified power law rate expression, shown in Table 4.34. The reactions follow second order kinetics: one order with respect to the nucleophilic reactant and one order with respect to the electrophilic reactant. Catalysts may make the reaction third order (one order with respect to catalyst).

The rate constants for the model-generated reactions are assumed to be on a functional group basis. The model applies correction factors to account for the number of like functional groups in each of the reactants. For example, in a reaction between a diol monomer and a diacid monomer, the specified rate constant is multiplied by four to account for the two acid groups in the diacid and the two alcohol groups in the diol.

Some reactions occur inside polymer chains at the intersection of two segments. The model applies a probability factor to estimate the concentration of the given segment pair. This probability is based on the most probable distribution. It assumes that the segments in the polymer alternate between nucleophilic segments and electrophilic segments. Repeat segments composed of an EN-GRP functional group behave as both nucleophiles and electrophiles, so these segments can alternate with themselves.

The standard rate expression is modified using the optional user rate constant feature. The rate constant form includes a parameter called the “user flag” which identifies an element in an array of user rate constants. This array is calculated by a user-written Fortran subroutine. The standard rate expression is multiplied by the user rate constants as shown in Table 4.34.

## *Table 4.34 Rate Expression for Model-Generated Reactions*

### Equation

$T_{ref}$ specified

$$rate = [Nucl][Elec] f_n f_e P \sum_i C_i k_{o\,i} e^{\frac{-Ea_i}{RT}\left(\frac{1}{T}-\frac{1}{T_{ref}}\right)} \left(\frac{T}{T_{ref}}\right)^{b_i} U\left(flag_i\right)$$

$T_{ref}$ unspecified

$$rate = [Nucl][Elec] f_n f_e P \sum_i C_i k_{o\,i} e^{\frac{-Ea_i}{RT}} T^{b_i} U\left(flag_i\right)$$

### Nomenclature

| Symbol | Description |
|---|---|
| [Nucl] | Concentration of the attacking nucleophilic species, mol/L* |
| [Elec] | Concentration of the attacking electrophilic species, mol/L* |
| $f_n$ | Number of electrophilic leaving groups in the attacking nucleophilic species. This factor is 2 for diol and diamine monomers. |
| $f_e$ | In reactions involving two victim species, $f_e$ is the number of electrophilic groups in the electrophilic species. This factor is 2 for repeat units which contain EE-GRP groups.<br>In reactions involving one victim species, $f_e$ is the number of nucleophilic leaving groups in the electrophilic species. This factor is 2 for diacid, diester, and carbonate monomers. |
| $P$ | In reactions involving two victim species, P is the probability of the victim nucleophilic species being adjacent to the victim electrophilic species. This probability factor is calculated by the model assuming the most probable distribution:<br>$P = \frac{f_{vns} N_{vns}}{\sum_i f_i N_i}$<br>where:<br>$f_{vns}$ = number of similar points of attachment in victim nucleophilic segment<br>(= 2 for NN-GRP repeat segments, 1 for all others)<br>$N_{vns}$ = concentration of victim nucleophilic segment<br>$i$ = index corresponding to list of all nucleophilic segments |
| $i$ | Index corresponding to the rate constant set number. The summation is performed over the specified list of rate constant set numbers. |
| $C_i$ | Catalyst concentration for rate constant set i. If the catalyst species is specified, this is the concentration of the species. If the catalyst group is specified, this the group concentration. If both species and group are specified, this is the concentration of the species times the number of the specified group in the specified species. If the catalyst is not specified, this factor is set to one. |
| $k_o$ | Pre-exponential factor in user-specified inverse-time units* |

* ***The concentration basis may be changed to other units using the optional concentration basis subroutine.***

*continued*

### *Table 4.34 Rate Expression for Model-Generated Reactions (cont.)*

| Symbol | Description |
|---|---|
| $Ea$ | Activation energy in user-specified mole-enthalpy units (default =0) |
| $b$ | Temperature exponent (default = 0) |
| $R$ | Universal gas constant in units consistent with the specified activation energy |
| $T$ | Temperature, K |
| $T_{ref}$ | Optional reference temperature. Units may be specified, and they are converted to K inside the model. |
| $flag$ | User flag for rate constant set i. This flag points to an element of the user rate constant array. |
| $U$ | User rate constant vector calculated by the optional user rate constant subroutine. The user flag indicates the element number in this array which is used in a given rate expression. When the user flag is not specified, or when the user rate constant routine is not present, this parameter is set to 1.0. |

* ***The concentration basis may be changed to other units using the optional concentration basis subroutine.***

## Assignment of Rate Constants to Model-Generated Reactions

Six qualifiers are used to assign each set of rate constants to internally-generated step-growth reactions, the:

- Attacking nucleophilic reactant name (A-NUCL-SPEC)
- Attacking electrophilic leaving group name (A-ELEC-GRP)
- Victim electrophilic reactant name (V-ELEC-SPEC)
- Victim nucleophilic group name (V-NUCL-GRP)
- Victim electrophilic species name (V-ELEC-SPEC)
- Victim electrophilic group name (V-ELEC-GRP)

Table 4.35 contains an example illustrating how these identifiers are used to distinguish between reactions. Note that the victim electrophilic species is only used for reactions which occur at the intersection of two segments in a polymer molecule.

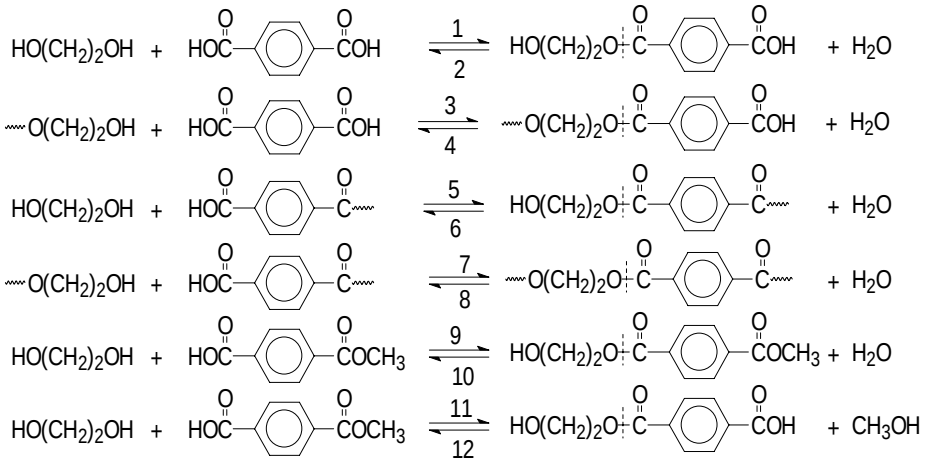
It is not necessary to specify all of the reaction identifiers. For example, the only time it is necessary to specify the attacking nucleophilic species and the attacking electrophilic group is when this species contains more than one type of group and the two groups are not equally reactive.

Sets of reactions may be grouped together by making more general specifications. For example, if the attacking electrophilic group and victim nucleophilic group are the only two identifiers specified, then the rate constants are assigned to all reactions involving the named groups.

When more than one reaction set is specified, the sets are processed in reaction set number order, e.g., reaction set one is processed before reaction set two, three, etc. When a match is found for a given reaction, the rate constant assignment algorithm moves to the next reaction, ignoring the remaining reaction sets. The algorithm is designed to find the "special cases" first, and then move on to the general cases.

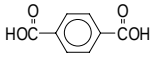
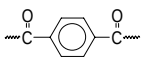
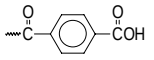
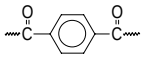
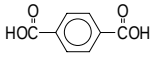
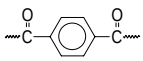
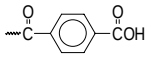
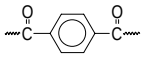
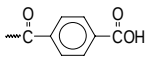
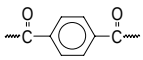
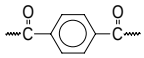
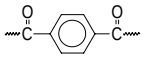
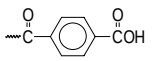
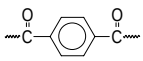
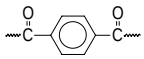
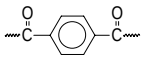
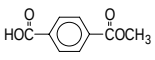
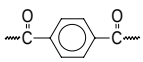
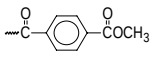
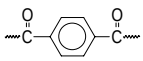
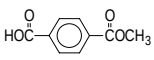
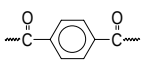
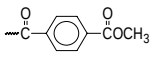
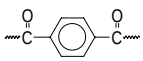
Several examples illustrating these concepts are included in Table 4.36. These examples are based on the set of reactions shown in Table 4.35.

### *Table 4.35 Reaction Identifiers for Step-Growth Reactions*

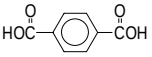
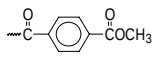


*continued*

## *Table 4.35 Reaction Identifiers for Step-Growth Reactions (cont.)*

| Reaction | Reaction Identifiers | | | | | |
|---|---|---|---|---|---|---|
| | Attacking Species | | Victim Species | | | |
| | A-Nucl-Spec | A-Elec-Grp | V-Elec-Spec | V-Elec-Grp | V-Nucl-Spec | V-Nucl-Grp |
| 1 | $HO(CH_2)_2OH$ | ~H in alcohol |  |  | none | ~OH in acid |
| 2 | $H_2O$ | ~H |  |  | $\sim O(CH_2)_2OH$ | $\sim O(CH_2)_2O\sim$ |
| 3 | $\sim O(CH_2)_2OH$ | ~H in alcohol |  |  | none | ~OH in acid |
| 4 | $H_2O$ | ~H |  |  | $\sim O(CH_2)_2O\sim$ | $\sim O(CH_2)_2O\sim$ |
| 5 | $HO(CH_2)_2OH$ | ~H in alcohol |  |  | none | ~OH in acid |
| 6 | $H_2O$ | ~H |  |  | $\sim O(CH_2)_2OH$ | $\sim O(CH_2)_2O\sim$ |
| 7 | $\sim O(CH_2)_2OH$ | ~H in alcohol |  |  | none | ~OH in acid |
| 8 | $H_2O$ | ~H |  |  | $\sim O(CH_2)_2O\sim$ | $\sim O(CH_2)_2O\sim$ |
| 9 | $HO(CH_2)_2OH$ | ~H in alcohol |  |  | none | ~OH in acid |
| 10 | $H_2O$ | ~H |  |  | $\sim O(CH_2)_2OH$ | $\sim O(CH_2)_2O\sim$ |
| 11 | $HO(CH_2)_2OH$ | ~H in alcohol |  |  | none | $\sim OCH_3$ |
| 12 | $CH_3OH$ | ~H |  |  | $\sim O(CH_2)_2OH$ | $\sim O(CH_2)_2O\sim$ |

## *Table 4.36 Examples: Rate Constant Assignment*

| Rxn-Sets | | Reaction Identifiers | | | | | |
|---|---|---|---|---|---|---|---|
| | **RC-Sets** | **A-Nucl-Spec** | **A-Elec-Grp** | **V-Elec-Spec** | **V-Elec-Grp** | **V-Nucl-Spec** | **V-Nucl-Grp** |
| Case 1 | Assign rate constant sets 1 and 2 to all of the model-generated reactions | | | | | | |
| 1 | 1, 2 | unspecified | unspecified | unspecified | unspecified | unspecified | unspecified |
| Case 2 | Assign rate constant sets 1 and 2 to reactions between alcohol groups in ethylene glycol and any acid groups<br>Assign rate constant sets 3 and 4 to reactions between alcohol groups in the polymer and any acid groups<br>Assign rate constant set 5 to reverse reactions involving methanol<br>Assign rate constant set 6 to reverse reactions involving water | | | | | | |
| 1 | 1, 2 | $HO(CH_2)_2OH$ | unspecified | unspecified | unspecified | unspecified | ~OH in acid |
| 2 | 3, 4 | $\sim O(CH_2)_2OH$ | unspecified | unspecified | unspecified | unspecified | ~OH in acid |
| 3 | 5 | $H_2O$ | unspecified | unspecified | unspecified | unspecified | unspecified |
| 4 | 6 | $CH_3OH$ | unspecified | unspecified | unspecified | unspecified | unspecified |
| Case 3 | Assign rate constant sets 1 and 2 to reactions between alcohol groups in ethylene glycol and terephthalic acid<br>Assign rate constant sets 3 and 4 to all other reactions involving acid groups<br>Assign rate constant set 5 to reactions between water and glycol end groups<br>Assign rate constant set 6 to all other reverse reactions involving water<br>Assign rate constant set 7 to reactions between ethylene glycol and the methylester end groups in the polymer<br>Assign rate constant 8 to all other reactions | | | | | | |
| 1 | 1, 2 | $HO(CH_2)_2OH$ | unspecified |  | unspecified | unspecified | unspecified |
| 2 | 3, 4 | unspecified | unspecified | unspecified | unspecified | unspecified | ~OH in acid |
| 3 | 5 | $H_2O$ | unspecified | unspecified | unspecified | $\sim O(CH_2)_2OH$ | unspecified |
| 4 | 6 | $H_2O$ | unspecified | unspecified | unspecified | unspecified | unspecified |
| 5 | 7 | $HO(CH_2)_2OH$ | unspecified |  | unspecified | unspecified | $\sim OCH_3$ |
| 6 | 8 | unspecified | unspecified | unspecified | unspecified | unspecified | unspecified |

## User Reactions

The model cannot predict all types of reactions based on the specified structures. Reactions which are not predicted by the model can be included as user-specified reactions. These can include thermal scission reactions, monomer or segment reformation, end-group modification, etc.

The user-specified reactions apply a modified power-law rate expression, as shown in Table 4.37. You can modify the standard rate expression using the optional user rate constant feature. The rate constant form includes a parameter called the "user flag" which identifies an element in an array of user rate constants. This array is calculated by a user-written Fortran subroutine. The standard rate expression is multiplied by the user rate constants as shown in Table 4.37.

*Conventional and Power-Law Components*

Conventional components and segments can appear as reactants or products in the reaction stoichiometry. Each reaction must be mass balanced (the mass of the products must be equal to the mass of the reactants).

The power-law components can include conventional components, segments, or oligomers. Power-law coefficients can be specified for components which do not appear in the reaction stoichiometry, such as catalysts or inhibitors.

The model allows the reactants to have power-law constants of zero, but this is not recommended because it can lead to numerical problems in the reactor models. For example, if a reaction "A→B" is zeroth order with respect to component "A", the reaction could have a positive rate even when component "A" is not present. This causes "non-negativity violation" integrator errors in RPLUG and RBATCH and causes convergence errors in RCSTR. To avoid these problems, specify a very small power-law coefficient, such as $1 \times 10^{-8}$.

A user-specified reaction can be accelerated by several different catalysts. In this situation, the entire reaction must be specified again for each catalyst in order to assign several sets of rate constants to the reaction.

When the side reaction kinetics are complicated, it can be easier to write the kinetics in the context of the available user kinetic subroutine. This subroutine is called from the Step-Growth reaction model. The argument list for this user-written Fortran subroutine includes the step-growth rate constants, user rate constants, species concentrations, group concentrations, species structures (number of each group in each species), and others.

### *Table 4.37 Rate Expression for User-Specified Reactions*

**Equation**

$T_{ref}$ specified $$rate = \left(\prod_j C_j^{a_{ij}}\right) k_{o\,i}\, e^{\frac{-Ea_i}{R}\left(\frac{1}{T}-\frac{1}{T_{ref}}\right)} \left(\frac{T}{T_{ref}}\right)^{b_i} U\left(flag_i\right)$$

$T_{ref}$ unspecified $$rate = \left(\prod_j C_j^{a_{ij}}\right) k_{o\,i}\, e^{\frac{-Ea_i}{RT}}\, T^{b_i} U\left(flag_i\right)$$

**Nomenclature**

| Symbol | Description |
|---|---|
| $i$ | User reaction number |
| $j$ | Component number |
| $\Pi$ | Product operator |
| $C_j$ | Concentration* of component j, mol/L |
| $\alpha_{ij}$ | Power-law exponent for component j in reaction i |
| $k_o$ | Pre-exponential factor in user-specified inverse-time units* |
| $Ea$ | Activation energy in user-specified mole-enthalpy units (default =0) |
| $b$ | Temperature exponent (default = 0) |
| $R$ | Universal gas constant in units consistent with the specified activation energy |
| $T$ | Temperature, K |
| $T_{ref}$ | Optional reference temperature. Units may be specified, they are converted to K inside the model. |
| $flag$ | User flag for rate constant set i. This flag points to an element of the user rate constant array. |
| $U$ | User rate constant vector calculated by the optional user rate constant subroutine. The user flag indicates the element number in this array which is used in a given rate expression. When the user flag is not specified, or when the user rate constant routine is not present, this parameter is set to 1.0. |

* ***The concentration basis may be changed to other units using the optional concentration basis subroutine.***

## User Subroutines

The Step-Growth model can be customized by applying user-written subroutines. There are three types of subroutines available. The concentration basis for the model can be changed through a user basis subroutine. This subroutine can also be used to calculate the volume (RCSTR and RBATCH) or area (RPLUG) of the reacting phase. A user rate-constant subroutine can be used to extend the standard rate expression for model-generated or user-specified reactions. A user kinetics routine can be used to add reactions to the model which are too difficult to represent using the power-law approach, or to calculate user attributes for polymer characteristics which are not tracked by Polymers Plus. These routines can be used together in any combination.

### User Basis Subroutine

The user basis subroutine can be used to calculate the component concentrations and the reacting-phase volume (area) basis used in the component and attribute conservation equations. Use this subroutine when rate constants are available in unusual concentration units not found in Polymers Plus, or when the reacting phase volume or area calculated by the reactor model is not consistent with the real reactor (for example, in plug flow reactors with fixed liquid level).

This subroutine can also be used in conjunction with Fortran blocks and user component attributes to calculate mass-transfer rates and to account for the influence of mass-transfer limitations on the component concentrations in the reacting phase.

The argument list for the user basis routine is in Table 4.38. This argument list is already prepared in a Fortran template called USRMTS.F, which is delivered with Polymers Plus.

Example 1 illustrates how to use the user basis routine to convert the concentration basis from the standard molar concentration basis (mol/L) to a mass concentration basis (mol/kg). Using these units, the reaction rates are calculated in units of mol/kg-sec. These rates are multiplied by the holdup basis (VBASIS) for the reactor in the Step-Growth model. For this reason, the holdup basis must be consistent with the concentration basis, e.g., it must be in kg. The holdup basis pertains to the reacting phase, it does not include the phases which do not react.

## Example 1: A User Basis Routine For the Mass-Concentration Basis

$$C_i = \frac{X_i}{\overline{M}_{Liquid}}$$

$C_i$ = mass-concentration of component *i*

$X_i$ = mole fraction of component *i*

$\overline{M}_{Liquid}$ = average molecular weight of components in the liquid phase

```
      CALL PPMON_VOLL( TEMP, PRES, X, NCPMX, IDXM,
     1             NBOPST, GLOBAL_LDIAG, 1, VLQ, DVS, KER)
C     - unpack the mole fraction vector into the molar concentrations...
      CALL SHS_UNPACK ( X , NCPMX, IDXM, CSS )
C -----------------------------------------------------------------------
C
C concentration (mole/kg) = ( mole i / mole liquid ) * ( mole liquid/kg)
C
C -----------------------------------------------------------------------
      DO 10 I = 1, NCOMP_NCC
        CSS(I) = CSS(I) * 1.D3 / STWORK_XMWL
 10   CONTINUE
C -----------------------------------------------------------------------
C
C reacting phase basis must be consistent with concentration basis (kg)
C liquid mass inventory = liquid volume * density
C
C -----------------------------------------------------------------------
      VBASIS = VLIQRX * STWORK_XMWL * 1.D-3 / VLQ
      RETURN
```

This excerpt does not include the argument list and declarations section of the user basis routine

The plug flow reactor model in Aspen Plus assumes that the vapor and liquid move at the same velocity through the reactor (e.g., no-slip conditions). This assumption is not consistent with the physical reality of polymer finishing reactors or wiped-film evaporators. The subroutine in Example 2 gets around the no-slip assumption in RPLUG, allowing you to specify the volume occupied by the liquid phase. In this example, the user specifies the first integer argument in the RPLUG block as “1” and specifies the first real argument as the volume fraction of the reactor occupied by the liquid phase.

## Example 2: A User Basis Routine to Specify Liquid Volume in RPLUG

```
      UFRAC = 1.D0
      IF ( REALB(1) .NE. RGLOB_RMISS ) UFRAC = REALB(1)
      IF ( INTB(1).EQ.1 ) THEN
C     - unpack the mole fraction vector into the molar concentrations...
        CALL SHS_UNPACK ( X , NCPMX, IDXM, CSS )
C     - concentration = mole fraction divided by molar volume of phase
        DO 20 I = 1, NCOMP_NCC
          CSS(I) = CSS(I) / VLQ
 20     CONTINUE
C     - multiply total reactor volume by user-specified volume fraction -
        VBASIS = ( VLIQRX + VVAPRX ) * UFRAC
C     - this line makes RPLUG calculate liquid residence time (not L+V)
        SOUT(NCOMP_NCC+8)=(SOUT(NCOMP_NCC+9)/SOUT(NCOMP_NCC+6)) / VLQ
        RETURN
      END IF
```

This excerpt does not include the argument list and declarations section of the user basis routine

## *Table 4.38 Argument List for the User Basis Subroutine*

### User Subroutine Arguments

```
      SUBROUTINE USRMTS
     1     SOUT,       NSUBS,      IDXSUB,     ITYPE,      XMW,
     2     IDSCC,      NPO,        NBOPST,     NIDS,       IDS,
     3     NINTB,      INTB,       NREALB,     REALB,      NINTM,
     4     INTM,       NREALM,     REALM,      NIWORK,     IWORK,
     5     NWORK,      WORK,       NCPM,       IDXM,       X,
     6     X1,         X2,         Y,          DUM1,       FLOWL,
     7     FLOWL1,     FLOWL2,     FLOWV,      FLOWS,      VLQ,
     8     VL1,        VL2,        VV,         VSALT,      VLIQRX,
     9     VL1RX,      VL2RX,      VVAPRX,     VSLTRX,     RFLRTN,
     *     IFLRTN,     CRATES,     NTCAT,      RATCAT,     CSS,
     1     VBASIS,     IPOLY,      NSEG,       IDXSEG,     AXPOS,
     2     TIME      )
```

### Argument Descriptions

| Variable | Usage | Type | Dimension | Description |
|---|---|---|---|---|
| SOUT | Input | REAL*8 | (1) | Stream vector |
| NSUBS | Input | INTEGER | | Number of substreams in stream vector |
| IDXSUB | Input | INTEGER | NSUBS | Location of substreams in stream vector |
| ITYPE | Input | INTEGER | NSUBS | Substream type vector<br>1=MIXED<br>2=CISOLID<br>3=NC |
| XMW | Input | REAL*8 | NCC | Conventional component molecular weights |
| IDSCC | Input | HOLLERITH | 2,NCC | Conventional component ID array |
| NPO | Input | INTEGER | | Number of property methods |
| NBOPST | Input | INTEGER | 6, NPO | Property method array |
| NIDS | Input | INTEGER | | Number of reaction model IDs |
| NINTB | Input | INTEGER | | User-specified length of INTB array |
| INTB | Retention | INTEGER | NINTB | Reactor block integer parameters (See Integer and Real Parameters) |
| NREALB | Input | INTEGER | | User-specified length of REALB array |
| REALB | Retention | REAL*8 | NREALB | Reactor block real parameters (See Integer and Real Parameters) |
| NINTM | Input | INTEGER | | User-specified length of INTM array |
| INTM | Retention | INTEGER | NINTM | User subroutine integer parameters (See Integer and Real Parameters) |

*continued*

### *Table 4.38 Argument List for the User Basis Subroutine (cont.)*

| Variable | Usage | Type | Dimension | Description |
|---|---|---|---|---|
| NREALM | Input | INTEGER | | User-specified length of REALM array |
| REALM | Retention | REAL*8 | NREALM | User subroutine real parameters (See Integer and Real Parameters) |
| NIWORK | Input | INTEGER | | Length of user subroutine integer work vector |
| IWORK | Work | INTEGER | NIWORK | User subroutine integer work vector (See Local Work Arrays) |
| NWORK | Input | INTEGER | | Length of user subroutine real work vector |
| WORK | Work | REAL*8 | NWORK | User subroutine integer work vector (See Local Work Arrays) |
| NCPM | Input | INTEGER | | Number of components present in the mixed substream (See Packed Vectors) |
| IDXM | Input | REAL*8 | NCPM | Component sequence numbers (See Packed Vectors) |
| X | Input | REAL*8 | NCPM | Overall liquid mole fractions |
| X1 | Input | REAL*8 | NCPM | First liquid mole fractions |
| X2 | Input | REAL*8 | NCPM | Second liquid mole fractions |
| Y | Input | REAL*8 | NCPM | Vapor phase mole fractions |
| Dum1 | Dummy | REAL*8 | (1) | Argument reserved for future application |
| FLOWL | Input | REAL*8 | | Total liquid flow rate, kmol/sec |
| FLOWL1 | Input | REAL*8 | | First liquid flow rate, kmol/sec |
| FLOWL2 | Input | REAL*8 | | Second liquid flow rate, kmol/sec |
| FLOWV | Input | REAL*8 | | Vapor flow rate, kmol/sec |
| FLOWS | Input | REAL*8 | | Salt flow rate, kmol/sec |
| VL | Input | REAL*8 | | Total liquid molar volume, $m^3$ / kmol |
| VL1 | Input | REAL*8 | | First liquid molar volume, $m^3$ / kmol |
| VL2 | Input | REAL*8 | | Second liquid molar volume, $m^3$ / kmol |
| VV | Input | REAL*8 | | Vapor molar volume, $m^3$ / kmol |
| VSALT | Input | REAL*8 | | Salt molar volume, $m^3$ / kmol |
| VLIQRX | Input | REAL*8 | | Volume* of liquid in reactor, $m^3$ |
| VL1RX | Input | REAL*8 | | Volume* of first liquid in reactor, $m^3$ |
| VL2RX | Input | REAL*8 | | Volume* of second liquid in reactor, $m^3$ |
| VVAPRX | Input | REAL*8 | | Volume* of vapor in reactor, $m^3$ |
| VSLTRX | Input | REAL*8 | | Volume* of salt in reactor, $m^3$ |

*continued*

***Table 4.38 Argument List for the User Basis Subroutine (cont.)***

| Variable | Usage | Type | Dimension | Description |
|---|---|---|---|---|
| RFLRTN | Retention | REAL*8 | (3, 1) | Real retention for FLASH |
| IFLRTN | Retention | INTEGER | (3, 1) | Integer retention for FLASH |
| CRATES | Output | REAL*8 | NCC | Component rates of change, kmol / $m^3$ - sec |
| NTCAT | Input | INTEGER | | Number of component attributes |
| RATCAT | Output | REAL*8 | NTCAT | Component attribute rates of change, cat / $m^3$ -sec |
| CSS | Output | REAL*8 | NCC | Concentration vector for the active phase |
| VBASIS | Output | REAL*8 | | Holdup basis used to calculate reaction rates* |
| IPOLY | Input | INTEGER | | Reacting polymer component index |
| NSEG | Input | INTEGER | | Number of segment components |
| IDXSEG | Input | INTEGER | NSEG | Segment component index vector |
| AXPOS | Input | REAL*8 | | RLUG only: axial position, m |
| TIME | Input | REAL*8 | | RBATCH only: time, sec |

* ***When using molar concentrations, this parameter is volume of the reacting phase in*** $m^3$ ***in RCSTR and RBatch or the cross-sectional area of the reacting phase in*** $m^2$ ***in RPlug.***

## User Rate-Constant Subroutine

The user rate constant subroutine can be used to modify rate constant parameters for model-generated and user-specified reactions. Use this routine to modify the standard power-law rate expression for non-ideal reaction kinetics.

The user rate constant feature can be used to modify the standard power-law rate expression. This subroutine returns a list of real values which are stored in an array “RCUSER”. The length of this array is defined by the keyword NURC (number of user rate constants) in the user rate constant subroutine form (USER-VECS secondary keyword). Each of the elements in the user rate constant array can store a different user rate constant. The USER-FLAG keyword in the SG-RATE-CON and RATE-CON forms is used to specify which user rate constant is used with a particular set of rate constants.

Elements 1-NURC of RCUSER are calculated by a user rate-constant subroutine. The standard rate expression is multiplied by the USER-FLAGth element of the user rate constant vector RCUSER. By default, the USER-FLAG keyword is set to zero. The zeroth element of the RCUSER array is set to a value of 1.0, so the rate expression remains unmodified unless the USER-FLAG keyword is specified.

The argument list for the subroutine is in Table 4.39. A Fortran template called USRRCS.F is delivered with Polymers Plus. Example 3 illustrates how to use this subroutine to implement complex rate expressions in the Step-Growth model.

## Example 3: Implementing a Non-Ideal Rate Expression

Suppose a side reaction $Q \rightarrow Z$ is first order with respect to component $Q$ and first order with respect to a catalyst $C$. The effectiveness of the catalyst is reduced by inhibitor $I$ according to the following equation:

$$[C_{eff}] = \frac{[C_{actual}]}{1 + (a + bT)[I]}$$

Where:

$[C_{eff}]$ = effective catalyst concentration, mol/L

$[C_{actual}]$ = actual catalyst concentration, mol/L

$[I]$ = inhibitor concentration, mol/L

$T$ = temperature, °K

$a, b$ = equation parameters

The net rate expression can thus be written as:

$$rate = [Q]\frac{[C_{actual}]}{1 + (a + bT)[I]} k_o e^{\frac{-E^*}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)}$$

Where:

$k_o$ = pre-exponential factor, (L/mol)/sec

$E^*$ = activation energy

$R$ = gas law constant

$T_{ref}$ = reference temperature for $k_o$

$[Q]$ = concentration of component $Q$, mol/L

*continued*

## Example 3: Implementing a Non-Ideal Rate Expression (cont.)

The standard rate expression for side reactions is:

$$rate = k_o e^{\frac{-E^*}{R}\left(\frac{1}{T}-\frac{1}{T_{ref}}\right)}\left(\prod_i C_i^{\alpha_i}\right) * U(j)$$

Where:

$\prod$ = product operator

$C_i$ = concentration of component *i*

$\alpha_i$ = power-law exponent for component *i*

$U$ = user rate constant

$j$ = user rate-constant flag

Suppose the rate constant for the uninhibited reaction is $3 \times 10^{-3}$ (L/mol)/min at 150°C, with an activation energy of 20 kcal/mol, and the inhibition rate constants are A=0.20 L/mol, B=0.001 L/mol-K. The stoichiometric coefficients and power-law exponents are specified directly in the Stoic and PowLaw-Exp keywords. The Arrehnius rate parameters and reference temperature are also specified directly in the model.

The parameters for the user rate constant equation can be specified using the optional REALRC list. Including the parameters in the REALRC list allows the model user to adjust these parameters using the standard variable accessing tools, such as Sensitivity, Design-Specification, and Data-Regression.

The resulting model input is summarized below:

```
USER-VECS NREALRC=2 NUSERRC=1
REALRC VALUE-LIST=0.2D0 0.001D0
STOIC 1      Q -1.0 / Z  1.0
POWLAW-EXP 1 Q  1.0 / C  1.0
RATE-CON 1 3D-3<1/MIN> 20.000<kcal/mol> TREF=150.0<C> URATECON=1
```

The power-law term from this equation is:

$$rate = k_o e^{\frac{-E^*}{R}\left(\frac{1}{T}-\frac{1}{T_{ref}}\right)}[C][Q]$$

Where:

[*Q*] = concentration of component *Q*, mol/L

[*C*] = catalyst concentration, mol/L

$k_o$ = pre-exponential factor

*continued*

## Example 3: Implementing a Non-Ideal Rate Expression (cont.)

Thus, the required user rate constant is:

$$U(j=1) = \frac{1}{(1+(a+bT)[I]}$$

Where:

[*I*] = inhibitor concentration, mol/L

*T* = temperature, K

*a*, *b* = equation parameters

An excerpt from the user rate constant subroutine for this equation is shown below:

```
C   - Component Name -
      INTEGER ID_IN(2)
      DATA ID_IN /'INHI','BITO'/
C ======================================================================
C     EXECUTABLE CODE
C ======================================================================
C   - find location of inhibitor in the list of components -
      DO 10 I = 1, NCOMP_NCC
       IF ( IDSCC(1,I).EQ.ID_IN(1).AND.IDSCC(2,I).EQ.ID_IN(2) ) I_IN=I
 10   CONTINUE
C   - get the concentration of the inhibitor -
      C_IN = 0.0D0
      IF ( I_IN .GT.0 ) C_IN  = CSS( I_IN )
C ----------------------------------------------------------------------
C     Parameters:  each REALR element defaults to zero if not specified
C ----------------------------------------------------------------------
      A = 0.0D0
      IF ( NREALR .GT. 0 ) A = REALR( 1 )
      B = 0.0D0
      IF ( NREALR .GT. 1 ) B = REALR( 2 )
C ----------------------------------------------------------------------
C     User rate constant #1  U(1) = 1 / ( 1 + (A+BT)[I] )
C ----------------------------------------------------------------------
      IF ( NURC.LT.1 ) GO TO 999
        RCUSER(1) = 1.0D0 / ( 1.0D0 + ( A + B*TEMP ) * C_IN )
      END IF
999   RETURN
```

### *Table 4.39 Argument List for the User Rate Constant Subroutine*

## User Subroutine Arguments

```
SUBROUTINE USRRCS
     1     SOUT,       NSUBS,      IDXSUB,     ITYPE,      XMW,
     2     IDSCC,      NPO,        NBOPST,     NIDS,       IDS,
     3     NINTB,      INTB,       NREALB,     REALB,      NINTR,
     4     INTR,       NREALR,     REALR,      NIWORK,     IWORK,
     5     NWORK,      WORK,       NCPM,       IDXM,       X,
     6     X1,         X2,         Y,          DUM1,       VL,
     7     VL1,        VL2,        VV,         VSALT,      IPOLY,
     8     NSEG,       IDXSEG,     NOLIG,      IDXOLI,     NSGOLG,
     9     NGROUP,     IDGRP,      NSPEC,      IDXSPC,     NFGSPC,
     *     CSS,        CGROUP,     TEMP,       PRES,       NURC,
     1     RCUSER      )
```

## Argument Descriptions

| Variable | Usage | Type | Dimension | Description |
|---|---|---|---|---|
| SOUT | Input | REAL*8 | (1) | Stream vector |
| NSUBS | Input | INTEGER | | Number of substreams in stream vector |
| IDXSUB | Input | INTEGER | NSUBS | Location of substreams in stream vector |
| ITYPE | Input | INTEGER | NSUBS | Substream type vector<br>1=MIXED<br>2=CISOLID<br>3=NC |
| XMW | Input | REAL*8 | NCC | Conventional component molecular weights |
| IDSCC | Input | HOLLERITH | 2, NCC | Conventional component ID array |
| NPO | Input | INTEGER | | Number of property methods |
| NBOPST | Input | INTEGER | 6, NPO | Property method array (used by FLASH) |
| NIDS | Input | INTEGER | | Number of reaction model IDs |
| IDS | Input | HOLLERITH | 2,NIDS | Reaction model ID list:<br>i,1 reactor block ID<br>i,2 reactor block type<br>i,3 reaction block ID<br>i,4 reaction block type<br>i,5 user subroutine ID |
| NINTB | Input | INTEGER | | User-specified length of INTB array |
| INTB | Retention | INTEGER | NINTB | Reactor block integer parameters (See Integer and Real Parameters) |

*continued*

### *Table 4.39 Argument List for the User Rate Constant Subroutine (cont.)*

| Variable | Usage | Type | Dimension | Description |
|---|---|---|---|---|
| NREALB | Input | INTEGER | | User-specified length of REALB array |
| REALB | Retention | REAL*8 | NREALB | Reactor block real parameters (See Integer and Real Parameters) |
| NINTR | Input | INTEGER | | User-specified length of INTM array |
| INTR | Retention | INTEGER | NINTR | User subroutine integer parameters (See Integer and Real Parameters) |
| NREALR | Input | INTEGER | | User-specified length of REALM array |
| REALR | Retention | REAL*8 | NREALR | User subroutine real parameters (See Integer and Real Parameters) |
| NIWORK | Input | INTEGER | | Length of user subroutine integer work vector |
| IWORK | Work | INTEGER | NIWORK | User subroutine integer work vector (See Local Work Arrays) |
| NWORK | Input | INTEGER | | Length of user subroutine real work vector |
| WORK | Work | REAL*8 | NWORK | User subroutine integer work vector (See Local Work Arrays) |
| NCPM | Input | INTEGER | | Number of components present in the mixed substream (See Packed Vectors) |
| IDXM | Input | REAL*8 | NCPM | Component sequence numbers (See Packed Vectors) |
| X | Input | REAL*8 | NCPM | Overall liquid mole fractions |
| X1 | Input | REAL*8 | NCPM | First liquid mole fractions |
| X2 | Input | REAL*8 | NCPM | Second liquid mole fractions |
| Y | Input | REAL*8 | NCPM | Vapor phase mole fractions |
| Dum1 | Dummy | REAL*8 | (1) | Argument reserved for future application |
| VL | Input | REAL*8 | | Total liquid molar volume, $m^3$ / kmol |
| VL1 | Input | REAL*8 | | First liquid molar volume, $m^3$ / kmol |
| VL2 | Input | REAL*8 | | Second liquid molar volume, $m^3$ / kmol |
| VV | Input | REAL*8 | | Vapor molar volume, $m^3$ / kmol |
| VSALT | Input | REAL*8 | | Salt molar volume, $m^3$ / kmol |
| IPOLY | Input | INTEGER | | Reacting polymer component index |
| NSEG | Input | INTEGER | | Number of segment components |
| IDXSEG | Input | INTEGER | NSEG | Segment component index vector |
| NOLIG | Input | INTEGER | | Number of oligomer components |
| IDXOLI | Input | INTEGER | NOLIG | Oligomer component index vector |

*continued*

***Table 4.39 Argument List for the User Rate Constant Subroutine (cont.)***

| Variable | Usage | Type | Dimension | Description |
|---|---|---|---|---|
| NSGOLG | Input | INTEGER | NSEG, NOLIG | Segment frequency vector: contains number of each segment in each oligomer |
| NGROUP | Input | INTEGER | | Number of functional groups |
| IDGRP | Input | HOLLERITH | NGROUP | Functional group ID vector |
| NSPEC | Input | INTEGER | | Number of reacting species |
| IDXSPC | Input | INTEGER | NSPEC | Reacting species component index vector |
| NFGSPC | Input | INTEGER | NSPEC, NGROUP | Group frequency vector: contains number of each functional group in each species |
| CSS | Input | REAL*8 | NCC | Concentration vector for reacting species |
| CGROUP | Input | REAL*8 | NGROUP | Concentration vector for reacting groups |
| TEMP | Input | REAL*8 | | Temperature, K |
| PRES | Input | REAL* | | Pressure, Pa |
| NURC | Input | INTEGER | | Number of user rate constants (See User Rate Constants) |
| RCUSER | Output | REAL*8 | NURC | User rate constant vector (see User Rate Constants) |

## User Kinetics Subroutine

The user kinetics subroutine is used to supplement the built-in kinetic calculations. Use this subroutine when the side reaction kinetics are too complicated to represent through the user rate constant routine, or when previously written Fortran routines are to be interfaced to the Step-Growth model. The argument list for this subroutine is in Table 4.40. The argument list and declarations are set up in a Fortran template called USRKIS.F which is delivered with Polymers Plus

The user kinetic subroutine returns the rate of change of the reacting species and the Class 2 component attributes (zeroth moment and segment flow rates). The subroutine may be applied to calculate user component attributes (CAUSRA etc.) to track color or other polymer properties which are related to the thermal history of the polymer.

Example 4 illustrates how the concentration of a color body can be tracked through user kinetics routine. The example assumes that the polymer color is proportional to the amount of unknown color bodies which are generated by side reactions. These unknown side reactions are sensitive to the thermal history of the polymer, according to an Arrehnius rate expression. The activation energy and pre-exponential factors of this expression are stored as the first and second REAL parameters for the user kinetics model.

### Example 4: Tracking Polymer Color Using User Attributes in a Step-Growth User Kinetics Model

```
     INTEGER IDUSRA(2)
     DATA IDUSRA /'CAUS','RA  '/
C.....GAS CONSTANT IN KCAL/MOL-K...
      RGASKC = 1.987D-3
C.....locate CAUSRA attribute:  LUSRA points to location in SOUT...
      LUSRA = SHS_LCATT( 1, IPOLY, IDUSRA )
C.....LURAT points to this attribute in the RATCAT vector...
      LURAT   = LUSRA - NCOMP_NVCP
C ---------------------------------------------------------------------
C     Get the rate constants from the list of REAL parameters in the
C     user-kinetics section of the Step-Growth Subroutine form
C     REAL(1)    A_CF    Color Formation pre-exponential, 1/min
C     REAL(2)    E_CF    Color Formation activation energy, kcal/mol-K
C ---------------------------------------------------------------------
      A_CF = 0.D0
      E_CF = 0.D0
      IF ( NREALK .GT. 1 ) THEN
         IF ( REALK( 1  ) .GE. RGLOB_RMISS ) REALK( 1  ) = 0.D0
         IF ( REALK( 2  ) .GE. RGLOB_RMISS ) REALK( 2  ) = 0.D0
         A_CF = REALK( 1  ) / 60.D0
         E_CF = REALK( 2  )
      END IF
C     Calculate color formation rate in color-units/cubic-meter/second
      RATCAT( LURAT ) = A_CF * DEXP( -E_CF / ( RGASKC*TEMP ) )
      RETURN
```

## Step-Growth Rate Constants

The step-growth reaction rate constants can be applied in the user kinetics subroutine. The rate constants are passed to this model as a set of arrays which are stored in rate constant set number order (the element number of the array corresponds to the reaction set number). These parameters are stored in SI units. The concentration basis for the pre-exponential factors are in molar concentration (mol/L) units. When a user concentration basis subroutine is used, the pre-exponential factors are assumed to be in units which are consistent with the user-calculated concentrations.

The user rate constants are also passed to the user kinetic subroutine. These parameters can be used “as is”, or they can be used with the step-growth rate constants to build rate expressions consistent with those used by the standard model. The array “UFLAG” is used to designate which user rate constant (if any) is assigned to a given set of step-growth rate constants. For example, if IUFLAG(2) = 1, then user rate constant 1 is assigned to step-growth rate constant set 2, and the pre-exponential factor can be adjusted accordingly. Example 5 illustrates how to apply user rate constants and step-growth rate constants in a user kinetics model.

### Example 5: How to Apply User Rate Constants and Step-Growth Rate Constant in a Step-Growth User Kinetics Model

```
C     set work space to calculate net rate constants
      LPREEX = 0
      LNETRC = LPREEX + NSGRC
C -----------------------------------------------------------------------
C    Multiply step-growth pre-exponential factors by user rate constants
C    and store the results in the work array.
C -----------------------------------------------------------------------
      DO 10 IR = 1, NSGRC
        IRCU = IUFLAG( IR )
        IF ( IRCU .EQ. 0 ) THEN
          WORK( LPREEX + IR ) = PREEXP( IR )
        ELSE
          WORK( LPREEX + IR ) = PREEXP( IR ) * RCUSER( IRCU )
        END IF
 10   CONTINUE
C -----------------------------------------------------------------------
C     Calculate the net rate constants
C -----------------------------------------------------------------------
      DO 20 IR = 1, NSGRC
        IF ( TREF(IR) .EQ. 0 ) THEN
          TTERM1 = 1/TEMP
          TTERM2 = TEMP**TEXP(IR)
        ELSE
          TTERM1 = 1/TEMP - 1/TREF(IR)
          TTERM2 = ( TEMP / TREF )**TEXP(IR)
        END IF
        ETERM = DEXP( -ACTNRG(IR) * TTERM1 / PPGLOB_RGAS )
        WORK( LNETRC+ IR  ) = WORK( LPREEX+ IR ) * ETERM * TTERM2
 20   CONTINUE
```

The work array is used to store intermediate results in the calculations. The size of the work array must be specified in the subroutine form and must be large enough to avoid overwriting the end of the array.

## INCL-COMPS List

The reactor models in Polymers Plus use mass-balance equations for each *reacting* component. In order to make the reactor models fast, components which do not appear in the reactions are excluded from these calculations.

The list of reacting components is automatically generated by the Step-Growth model. This list includes the polymer component, listed oligomers, components which appear in the list of reacting species, components which appear as products or reactants in the user-specified reactions, and components in the INCL-COMPS component list.

When user concentration basis or user kinetics subroutines are applied in a model, these subroutines can include reactions involving components which do not otherwise appear in the list of reacting components. These components should be added to the INCL-COMPS list to ensure they appear in the mass-balance equations.

### *Table 4.40 Argument List for Step-Growth User Kinetic Subroutine*

## User Subroutine Arguments

```
SUBROUTINE USRKIS(
     1     SOUT,       NSUBS,      IDXSUB,     ITYPE,      XMW,
     2     IDSCC,      NPO,        NBOPST,     NIDS,       IDS,
     3     NINTB,      INTB,       NREALB,     REALB,
     4     NINTK,      INTK,       NREALK,     REALK,      NIWRK,
     5     IWRK,       NWRK,       WRK,        NCPMX,      IDXM,
     6     X,          X1,         X2,         Y,          DUMXS,
     7     FLOWL,      FLOWL1,     FLOWL2,     FLOWV,      DUMFS,
     8     VLQ,        VLQ1,       VLQ2,       VVP,        VOLSLT,
     9     VLIQRX,     VL1RX,      VL2RX,      VVAPRX,     VSLTRX,
     *     IPOLY,      NSEG,       IDXSEG,     NOLIG,      IDXOLI,
     1     NSGOLG,     NGROUP,     IDGRP,      NSPEC,      IDXSPC,
     2     NFGSPC,     CSS,        CGROUP,     TEMP,       PRES,
     3     RFLRTN,     IFLRTN,     CRATES,     NTCAT,      RATCAT,
     4     NRC,        PREEXP,     ACTNRG,     TEXP,       TREF,
     5     IUFLAG,     NURC,       RCUSER )
```

## Argument Descriptions

| Variable | Usage | Type | Dimension | Description |
|---|---|---|---|---|
| SOUT | Input | REAL*8 | (1) | Stream vector |
| NSUBS | Input | INTEGER | | Number of substreams in stream vector |
| IDXSUB | Input | INTEGER | NSUBS | Location of substreams in stream vector |
| ITYPE | Input | INTEGER | NSUBS | Substream type vector<br>1=MIXED<br>2=CISOLID<br>3=NC |
| XMW | Input | REAL*8 | NCC | Conventional component molecular weights |
| IDSCC | Input | HOLLERITH | 2, NCC | Conventional component ID array |
| NPO | Input | INTEGER | | Number of property methods |
| NBOPST | Input | INTEGER | 6, NPO | Property method array (used by FLASH) |
| NIDS | Input | INTEGER | | Number of reaction model IDs |
| IDS | Input | HOLLERITH | 2,NIDS | Reaction model ID list:<br>i,1 reactor block ID<br>i,2 reactor block type<br>i,3 reaction block ID<br>i,4 reaction block type<br>i,5 user subroutine ID |

*continued*

### *Table 4.40 Argument List for Step-Growth User Kinetic Subroutine (cont.)*

| Variable | Usage | Type | Dimension | Description |
|---|---|---|---|---|
| NINTB | Input | INTEGER | | User-specified length of INTB array |
| INTB | Retention | INTEGER | NINTB | Reactor block integer parameters (See Integer and Real Parameters) |
| NREALB | Input | INTEGER | | User-specified length of REALB array |
| REALB | Retention | REAL*8 | NREALB | Reactor block real parameters (See Integer and Real Parameters) |
| NINTK | Input | INTEGER | | User-specified length of INTM array |
| INTK | Retention | INTEGER | NINTK | User subroutine integer parameters (See Integer and Real Parameters) |
| NREALK | Input | INTEGER | | User-specified length of REALM array |
| REALK | Retention | REAL*8 | NREALK | User subroutine real parameters (See Integer and Real Parameters) |
| NIWORK | Input | INTEGER | | Length of user subroutine integer work vector |
| IWORK | Work | INTEGER | NIWORK | User subroutine integer work vector (See Local Work Arrays) |
| NWORK | Input | INTEGER | | Length of user subroutine real work vector |
| WORK | Work | REAL*8 | NWORK | User subroutine integer work vector (See Local Work Arrays) |
| NCPM | Input | INTEGER | | Number of components present in the mixed substream (See Packed Vectors) |
| IDXM | Input | REAL*8 | NCPM | Component sequence numbers (See Packed Vectors) |
| X | Input | REAL*8 | NCPM | Overall liquid mole fractions |
| X1 | Input | REAL*8 | NCPM | First liquid mole fractions |
| X2 | Input | REAL*8 | NCPM | Second liquid mole fractions |
| Y | Input | REAL*8 | NCPM | Vapor phase mole fractions |
| Dum1 | Dummy | REAL*8 | (1) | Argument reserved for future application |
| FLOWL | Input | REAL*8 | | Total liquid flow rate, kmol / sec |
| FLOWL1 | Input | REAL*8 | | First liquid flow rate, kmol / sec |
| FLOWL2 | Input | REAL*8 | | Second liquid flow rate, kmol / sec |
| FLOWV | Input | REAL*8 | | Vapor flow rate, kmol / sec |
| FLOWS | Input | REAL*8 | | Salt flow rate, kmol / sec |
| VL | Input | REAL*8 | | Total liquid molar volume, $m^3$ / kmol |
| VL1 | Input | REAL*8 | | First liquid molar volume, $m^3$ / kmol |
| VL2 | Input | REAL*8 | | Second liquid molar volume, $m^3$ / kmol |

*continued*

### *Table 4.40 Argument List for Step-Growth User Kinetic Subroutine (cont.)*

| Variable | Usage | Type | Dimension | Description |
|---|---|---|---|---|
| VV | Input | REAL*8 | | Vapor molar volume, $m^3$ / kmol |
| VSALT | Input | REAL*8 | | Salt molar volume, $m^3$ / kmol |
| VLIQRX | Input | REAL*8 | | Volume* of liquid in reactor, $m^3$ |
| VL1RX | Input | REAL*8 | | Volume* of first liquid in reactor, $m^3$ |
| VL2RX | Input | REAL*8 | | Volume* of second liquid in reactor, $m^3$ |
| VVAPRX | Input | REAL*8 | | Volume* of vapor in reactor, $m^3$ |
| VSLTRX | Input | REAL*8 | | Volume* of salt in reactor, $m^3$ |
| IPOLY | Input | INTEGER | | Reacting polymer component index |
| NSEG | Input | INTEGER | | Number of segment components |
| IDXSEG | Input | INTEGER | NSEG | Segment component index vector |
| NOLIG | Input | INTEGER | | Number of oligomer components |
| IDXOLI | Input | INTEGER | NOLIG | Oligomer component index vector |
| NSGOLG | Input | INTEGER | NSEG, NOLIG | Segment frequency vector: contains number of each segment in each oligomer |
| NGROUP | Input | INTEGER | | Number of functional groups |
| IDGRP | Input | HOLLERITH | 2,NGROUP | Functional group ID vector |
| NSPEC | Input | INTEGER | | Number of reacting species |
| IDXSPC | Input | INTEGER | NSPEC | Reacting species component index vector |
| NFGSPC | Input | INTEGER | NSPEC, NGROUP | Group frequency vector: contains number of each functional group in each species |
| CSS | Input | REAL*8 | NCC | Concentration vector for reacting species |
| CGROUP | Input | REAL*8 | NGROUP | Concentration vector for reacting groups |
| TEMP | Input | REAL*8 | | Temperature, K |
| PRES | Input | REAL* | | Pressure, Pa |
| RFLRTN | Retention | REAL*8 | 3,(1) | Real retention for FLASH |
| IFLRTN | Retention | INTEGER | 3,(1) | Integer retention for FLASH |
| CRATES | Output | REAL*8 | NCC | Component rates of change, kmol / $m^3$ -sec |
| NTCAT | Input | INTEGER | | Total number of component attributes |
| RATCAT | Output | REAL*8 | NTCAT | Component attribute rates of change, cat / $m^3$ -sec |

***Area in RPLUG***

*continued*

***Table 4.40 Argument List for Step-Growth User Kinetic Subroutine (cont.)***

| Variable | Usage | Type | Dimension | Description |
|---|---|---|---|---|
| NSGRC | Input | INTEGER | | Number of sets of step-growth rate constants |
| PREEXP | Input | REAL*8 | NSGRC | Pre-exponential factors, 1/sec (see Step-Growth Rate Constants) |
| ACTNRG | Input | REAL*8 | NSGRC | Activation energies, J/kmol-K |
| TEXP | Input | REAL*8 | NSGRC | Temperature exponents, unitless |
| TREF | Input | REAL*8 | NSGRC | Reference temperatures, K |
| IUFLAG | Input | Integer*8 | NSGRC | User rate constant flags (see User Rate Constants) |
| NURC | Input | INTEGER | | Number of user rate constants |
| RCUSER | Output | REAL*8 | NURC | User rate constant vector (see User Rate Constants) |

## Integer and Real Parameters

Each user model has two sets of integer and real parameters. The first set comes from the subroutine form of the reactor block. The second set comes from the subroutine form of the step-growth reactions model. Each of these parameters are retained from one call to the next, thus these parameters can be used as model inputs, outputs, or retention.

The reactor block integer and real parameters can be used to specify data which are specific to a particular unit operation, such as reactor geometry, mass transfer coefficients, etc. The integer and real parameters in the subroutine forms can be used to specify global parameters, such as rate constants or physical property parameters.

## Local Work Arrays

You can use local work arrays by specifying the model workspace array length on the STEP-GROWTH Subroutine form. These work areas are not saved from one call to the next. All three user subroutines share a common work area, so you must zero out the work space at the start of each subroutine.

## Packed Vectors

Aspen Plus frequently uses a technique called “packing” to minimize simulation time. The user models previously described use packed vectors to track the mole fractions of each phase (vectors X, X1, X2, and Y). These vectors contain NCPM elements (Number of Components Present in the Mixed substream). The component index associated with each element is listed in the vector ✌IDXM✍. All other vectors used by the model, including the rates vectors and the component concentration vectors, are unpacked.

### Example 6: Calculating Unpacked Component Concentrations

Calculate unpacked component concentrations of the first liquid phase given the packed mole fractions of the first liquid phase and the molar volume of the first liquid phase.

```
IF ( VL1 .GT. 0.D0 .AND. FLOWL1.GT.0.D0 ) THEN
    DO 10 I = 1, NCPM
    CSS(I) = X1( IDXM( I ) ) / VL1
 10   CONTINUE
END IF
```

NCPM steps were required to load the concentration vector. Since NCPM is always less than or equal to NCC (total number of conventional components), there is a reduction in the required number of steps to perform the operation.

# SPECIFYING STEP-GROWTH POLYMERIZATION KINETICS

## Accessing the Step-Growth Model

To access the Step-Growth polymerization kinetic model:

1. From the Data Browser, find the **Reactions** folder.
2. From the **Reactions** folder, select **Reactions** again to get to the Reactions object manager.

   If the kinetic model already exists, double-click on the desired Reaction ID in the object manager or select **Edit** to get to the input forms.
3. To add a new model, from the **Reactions** object manager, select **New**. If necessary, change the default ID for the reaction.
4. Select Step-Growth as the reaction type and click on **OK**.

## Specifying the Step-Growth Model

The Step-Growth model input forms are divided into two folders: Specifications and User Subroutines.

Use the **Specifications** forms to define reacting species and functional groups, enter reaction rate constant parameters, and include user side reactions. Use the following options:

| Use this sheet | To |
|---|---|
| Species | Define reacting species and functional groups |
| | Specify the name of the polymer being produced |
| | Specify the names for linear oligomers (optional) |
| Reactions | Generate and display model-generated reactions |
| Rate Constants | Specify reaction rate constants for model-generated reactions |
| User Reactions | Specify reaction stoichiometry and enter rate constants for user-specified reactions |
| Report | Select report options for internally generated reactions |

Use the **User Subroutines** forms to define reacting species and functional groups, enter reaction rate constant parameters, and include user side reactions. Use the following options:

| Use this sheet | To |
|---|---|
| Kinetics | Specify the name of the user kinetics routine and give the integer and real arguments for the user arrays for this routine |
| Rate Constants | Specify the name of the user kinetics routine, the number of user rate constants calculated by the routine, and to give the integer and real arguments for the user arrays for this routine |
| Basis | Specify the name of the user concentration and reacting phase volume basis routine and give the integer and real arguments for the user arrays for this routine |

## Specifying Reacting Components

You must specify the reacting species and functional groups on the Step-Growth **Specifications Species** sheet.

First specify the polymers and oligomers produced:

1. In the **Polymer** field, specify the polymer produced.
2. In the **Oligomers** field list oligomers which you want tracked by the model.
3. In the species definition table specify the functional groups contained in each reacting species and define each group type.

The structure of reacting species in terms of the reactive functional groups they contain must be defined. To do this:

1. In the **Group** field specify an ID name for each functional group type present in the reacting species.
2. For each group, select a type from the group type field.
3. List the species in the **Species** field.

   These species may be monomers, condensates, or segments.
4. The resulting form is a spreadsheet, with each column representing a functional group and each row representing a reacting species. The cells in the spreadsheet correspond to the number of each functional group in each species.

   For each species, specify in the number field the number of each defined functional group contained in that species.

   Unspecified fields are interpreted as zeros.

## Listing Built-In Reactions

The step-growth model generates reactions based on the functional group definition of reacting species. You can view the system-generated reactions, by clicking on the **Generate Reactions** button on the Specifications Reactions tab sheet.

In the Reaction summary listing, for each reaction the first column indicates the reaction type. The second column lists the reactants, and the last column lists the products. The Data Browser window can be resized to better view the reaction listing.

## Specifying Built-In Reaction Rate Constants

You can define the catalysts and rate constants for system-generated reactions. The model applies a modified power-law rate expression, which can be customized through a user-written rate constant subroutine. By default, the model assumes concentrations are in mol/liter. Another concentration basis can be applied through a user-written basis subroutine.

To specify rate constants:

1. Go to the **Rate constants** tab sheet.
2. In the reaction **No.** field assign a unique integer identifier for a set of rate constant parameters.
3. In the **Catalyst Species** field, specify the name of a catalyst species associated with the rate constant set.

   You may leave this field unspecified if the reaction is uncatalyzed, or if the catalyst is defined as a functional group.
4. In the **Catalyst Group** field, specify the name of a catalyst functional group associated with the rate constant set.

   You may leave this field unspecified if the reaction is uncatalyzed, or if the catalyst is defined as a species.
5. Enter the rate constant parameters: **ko** for Pre-exponential factor, **Ea** for Activation energy, **b** for Temperature exponent, **Tref** for Reference temperature.
6. Request any user rate constant expression in the **User flag** field.
7. Repeat these steps as needed to specify the list of rate constant parameters.

## Assigning Rate Constants to Reactions

You can assign rate constants to individual reactions using the reaction stoichiometry, or you can assign rate constants to sets or reactions using the appropriate reaction identifiers.

To assign the rate constants set:

1. Click on the **Assign Rate Constants** button on the Specifications Rate constants tab sheet.
2. Click on the **Global** tab to assign rate constants to a set of reactions or use the **Individual** sheet to assign rate constants to individual reactions.
3. Go to the **Rate Constant Sets** field, select from the list of pre-defined rate constant sets for each reaction.

## Including User Reactions

You can add user reactions to the built-in set. For this you must specify a reaction stoichiometry and the associated rate constants. The model applies a modified rate expression, which can be customized through a user-written rate constant subroutine.

To add user reactions use the following options found on the Specifications User Reactions tab sheet:

| Click on | To |
|---|---|
| New | Add new reactions to the scheme |
| Edit | Edit the current reaction indicated by the row selector |
| Rate Constants | Specify reaction rate constant parameters for the reactions |

Click to select a reaction. Click a reaction then Control-Click to include additional reactions for multiple selection. Double-click to edit a reaction.

In addition, you may use the following buttons:

| Click on | To |
|---|---|
| Hide/Reveal  | Exclude/Include a reaction from the calculations |
| Delete  | Permanently remove a reaction from the model |

## Adding or Editing User Reactions

In the **User Reactions** sheet, to add a new reaction to the scheme or edit an existing reaction open the Edit subform. When you open the Edit subform, in the **Reaction no.** field, a unique number is assigned to the reaction being added.

1. Specify the **Component ID** and stoichiometric **Coefficient** for the reactants. Reactants must have a negative coefficient.
2. Specify the **Component ID** and stoichiometric **Coefficient** for the products. Products must have a positive coefficient.
3. Click on the N→ to check the **Completion Status**

   – or –

   Click **Close** to return to the reaction summary.

## Assigning Rate Constants to User Reactions

To assign rate constants to user reactions, on the **User Reactions** tab, click on **Rate Constants** button to open the Rate Constant Parameters subform:

1. In the $k_o$ field, enter the pre-exponential factor.
2. In the $E_a$ field, enter the activation energy.
3. In the **b** field, enter the temperature exponent.
4. In the $T_{ref}$ field, enter the reference temperature.
5. Click on the stoichiometry list and select a new reaction to enter rate constants for another reaction.
6. Click on **Close** to return to the reaction summary.

## Selecting Report Options

You can select which format to use for the step-growth reactions in the report file. Select **Report** to request a reaction report. Then select a **Summary** format or **Detailed** format.

## Including a User Kinetic Subroutine

Use the **User Subroutines Kinetics** form to specify parameters for user kinetics calculations:

1. In subroutine **Name**, enter the name of the Fortran subroutine.
2. Specify the size of vectors for **Integer**, **Real** in **Number of parameters**, and **Length of work arrays**.
3. Enter integer and real parameter values in **Values for parameters** columns.
4. Click on **Include Comps** to specify components to be included in material balance convergence.

## Including a User Rate Constant Subroutine

Use the User Subroutines Rate Constants form to specify parameters for user rate constants calculations:

1. In subroutine **Name**, enter the name of the Fortran subroutine.
2. Specify the size of vectors for **Integer**, **Real** and **No. const.** in **Number of parameters**.
3. Specifying the size of vectors of **Integer** and **Real** in **Length of work arrays**.
4. Enter integer and real parameter values in **Values for parameters** columns.

## Including a User Basis Subroutine

Use the User Subroutines Basis form to specify parameters for basis calculations:

1. In subroutine **Name**, enter the name of the Fortran subroutine.
2. Specify the size of vectors for **Integer** and **Real** in the **Number of parameters** and **Length of work arrays**.
3. Enter integer and real parameter values in **Values for parameters** columns.

# REFERENCES

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Kaufman, H. S., and J. J. Falcetta ed., Introduction to Polymer Science and Technology: An SPE Textbook, Wiley, New York (1977).

McKetta, J. J., ed., Encyclopedia of Chemical Processing and Design, **39** & **40**, Marcel Dekker, New York (1992).

Rodriguez, F., Principles of Polymer Systems, Hemisphere, New York (1989).

# 4.2 FREE-RADICAL BULK POLYMERIZATION

This section covers the free-radical bulk/solution polymerization model available in Polymers Plus.

Topics covered include:

- Summary of Applications
- Free-Radical Bulk/Solution Processes
- Reaction Kinetic Scheme
- Model Features and Assumptions
- Polymer Properties Calculated
- Specifying Free-Radical Polymerization Kinetics

Several example applications of the free-radical bulk/solution polymerization model are given in the *Polymers Plus Examples & Applications Case Book*. The *Examples & Applications* provide process details and the kinetics of polymerization for specific monomer-polymer systems.

# SUMMARY OF APPLICATIONS

The free-radical bulk/solution polymerization model is applicable to bulk and solution polymerization processes. Some examples of applicable polymers are:

- General purpose polystyrene - Made by polymerization of styrene monomer with or without solvent fed continuously to reactor.
- High impact polystyrene - Made by polymerization of an unsaturated rubber dissolved in styrene in a solution process. Also produced in mass-suspension processes.
- Poly(vinyl chloride) - Produced in bulk polymerization using monomer-soluble free radical initiators. Most of the homopolymers and copolymers of vinyl chloride, however, are produced by suspension polymerization.
- Poly(vinyl acetate) - Produced industrially by the polymerization of vinyl acetate in bulk or solution processes. Also produced in suspension and emulsion processes. Both batch and continuous processes are used.
- Poly(vinyl alcohol) - Poly(vinyl acetate) is converted into the corresponding poly(vinyl alcohol) by direct hydrolysis or catalyzed alcoholysis. The reaction can be catalyzed by strong acids or strong bases.
- Poly(methyl methacrylate) - The vast majority of commercially prepared acrylic polymers and methacrylic polymers are copolymers. Commercially they are prepared by solution polymerization. They are also produced by emulsion polymerization and suspension polymerization.
- Low density polyethylene - Made by high pressure, free radical processes in either a tubular reactor or a stirred autoclave. Typical commercial processes include staged compression, initiator injection, partial conversion of ethylene to polymer, separation of ethylene from polymer, extrusion of molten polymer, and cooling of ethylene.

# FREE-RADICAL BULK/SOLUTION PROCESSES

Free-radical polymerization accounts for a large proportion (more than 40% by weight) of the commodity grade polymers. It is employed in the synthesis of countless homo- and copolymers using monomers that are either monosubstituted ethylenes $\left(RHC=CH_2\right)$ or 1,1-disubstituted ethylenes $\left(R_1R_2C=CH_2\right)$.

Free-radical polymerization usually takes place with the monomer in the liquid phase. Several types of processes are used. A solvent or suspending medium may be used, and the polymer formed may be soluble, insoluble, or swelled by the monomer and solvent. Commercially important processes for free-radical polymerization include bulk, solution, suspension, and emulsion polymerization.

*Bulk and Solution Polymerization*

Bulk and solution polymerization processes are characterized by the fact that the reactions proceed in a single phase. Typically the monomers are fed to a reactor with or without a solvent. A small amount of initiator is also fed. At the reaction temperature, the initiator decomposes to form radicals that initiate the polymerization reactions. The polymer formed is usually soluble in the monomer/solvent mixture. However, in some systems, such as PVC, the polymer is insoluble and forms a separate phase.

The most commonly used reactor types include batch, semi-batch, continuous stirred-tank and tubular reactors. Flowsheets consisting of several reactors in series are common. The main technical challenges with bulk/solution polymerization processes are heat removal, handling of the highly viscous liquid, and recovery of residual monomer/solvent. Several modes of heat removal can be employed, including jacket cooling, internal cooling coils/baffles, external heat exchangers and reflux condensors.

# REACTION KINETIC SCHEME

Most free-radical polymerizations have at least four basic reaction steps:

- Initiation
- Propagation
- Chain transfer to a small molecule (i.e. monomer, solvent or transfer agent)
- Termination

These reactions occur simultaneously during the polymerization. For branched polymers additional reactions for long and short chain branching can also be present. A comprehensive kinetic scheme for the free-radical homo- and copolymerization of up to $N_m$ monomers has been built into Polymers Plus. The built-in kinetic scheme is in Figure 4.6. The scheme includes most of the reactions commonly used for modeling free-radical polymerization. Reactions such as depropagation, internal or terminal double-bond polymerization, and random chain scission have not been included in the current model. These reactions may be added to the built-in scheme in the future.

The nomenclature used in the kinetic scheme is in Table 4.41. In the discussion below, a polymer chain is considered to be made up of monomer units or segments derived from the propagating monomers. Typically there will be one segment type associated with each monomer. However, it is possible to define several segment types associated with a single monomer. This may be necessary, for example, for modeling the tacticity of a polymer, or head-to-head versus head-to-tail incorporation of an asymmetric monomer $\left(RHC = CH2\right)$.

*Polymer Chain Terms*

The term *live polymer chain* $(P_n^i)$ refers to growing polymer chains containing *n* segments, with a radical attached to a segment of type *i*, i.e., segment formed from monomer *i*. The term *dead polymer chain* $(D_n)$ refers to terminated polymer chains that do not have an attached radical. The term *bulk polymer chain* is used to refer to the sum of the live and dead polymer chains. The subscript *n* refers to the chain length in terms of the number of segments or monomer units incorporated in the polymer chain. Live chains are reactive and can participate in the polymerization reactions while dead chains are usually considered inert, except when long chain branching reactions are important.

The radical attached to one end of a live polymer chain is considered to be mobile and moves away from the initiator fragment with every addition of a monomer molecule. It is believed that after a few monomer additions the chemistry of the initiator fragment and developing chain microstructure will not have a strong influence on the mode of monomer addition.

The free-radical kinetic model assumes that the reactivity of a live polymer chain depends only on the active segment containing the radical, and is independent of the polymer chain length and other structural properties. This assumption was used in writing the rate expressions for the reactions in Figure 4.6. For example, in the propagation reaction, the rate of propagation $(R_p^{ij})$ is independent of the polymer chain length. It depends only on the concentration of monomer *j* and the concentration of live polymer chains with active segments of type *i*. Models using this assumption are referred to as *terminal models* in the polymerization literature.

For copolymerization, the built-in kinetics routine allows the user to specify the number of monomers used. Similarly, the user has the flexibility to specify the number of each type of reactive species used in the polymerization, e.g. initiators, chain transfer agents, solvents and inhibitors. The user can easily setup the built-in kinetics to model a specific free-radical polymerization by selecting a subset of the reactions in Figure 4.6. It is necessary that the subset include a chain initiation and a propagation reaction. Frequently, at least one termination, chain transfer, or inhibition reaction to produce dead polymer is also selected.

The rate constants for each reaction in the built-in kinetics is calculated at the reaction temperature and pressure using the modified Arrhenius equation shown below with user specified parameters: pre-exponential (or frequency) factor, activation energy and activation volume:

*Rate Constant*

$$k = k_o \exp\left(\frac{-Ea}{RT} - \frac{\Delta VP}{RT}\right) \qquad \textbf{(4.1)}$$

Where:

$k_o$ = pre-exponential factor in l/sec for first order reactions, and $m^3 / kmol - s$ for second order reactions

$Ea$ = activation energy in mole-enthalpy units

$\Delta V$ = activation volume in volume/mole units

$P$ = reaction pressure

$R$ = universal gas constant

$T$ = reaction temperature

The second term in the exponential function contains an activation volume which is important for high pressure polymerization systems. For low to moderate pressures, the activation volume is typically set to default value of zero. This term is used to account for the pressure dependence of the reaction rate constant.

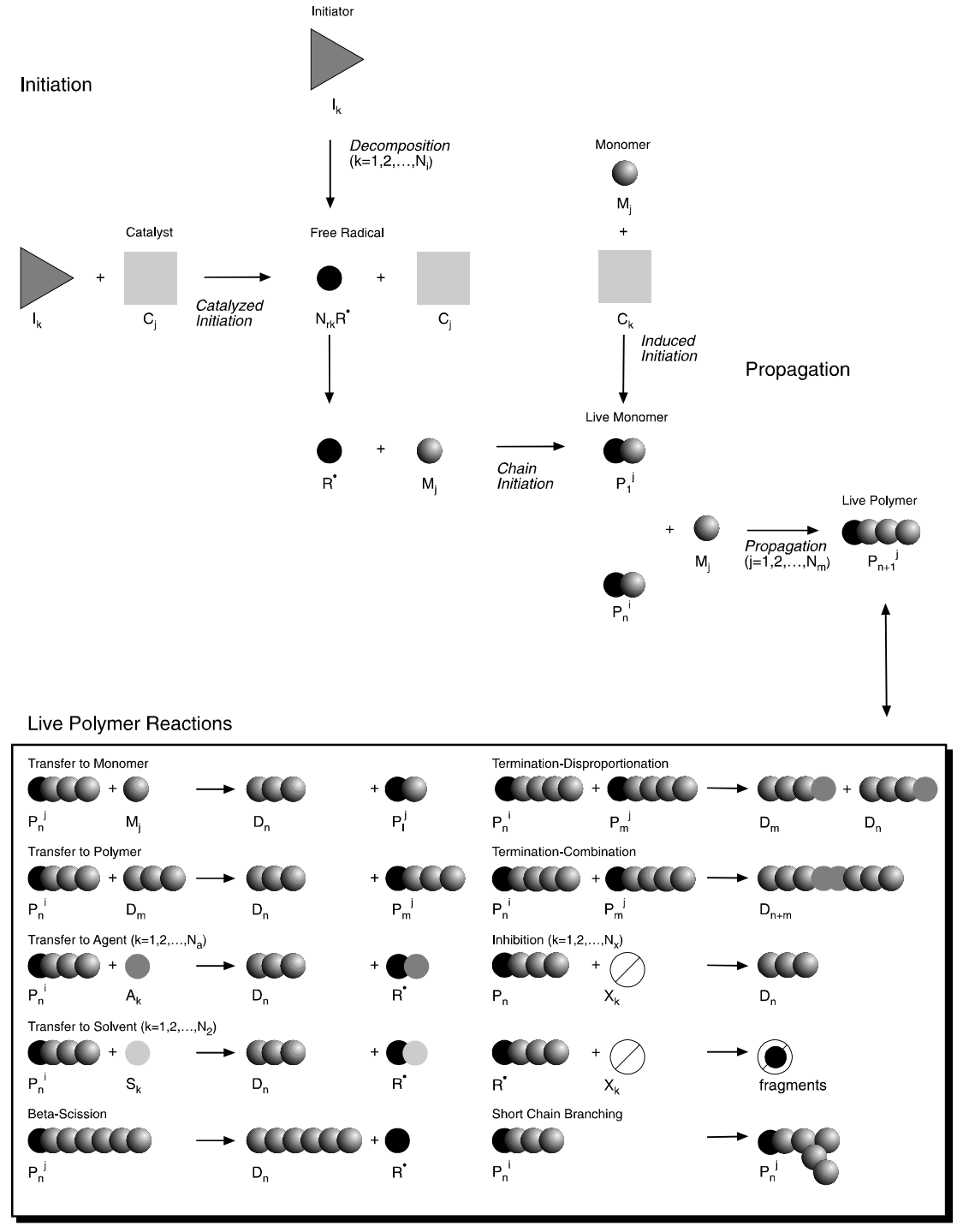


***Figure 4.6*** *Built-in Free-Radical Polymerization Kinetic Scheme*

### *Table 4.41 Free-Radical Polymerization Kinetics Nomenclature*

| Symbol | Description |
|---|---|
| $A_k$ | Chain transfer agent of type k |
| $a,\ b,\ c$ | Coefficients for the induced (thermal, radiation) initiation rate |
| $C_k$ | Coinitiator or catalyst of type k |
| $D_n$ | Dead polymer chain of length n $(= n1,\ n2,\ \ldots n_m)$ for copolymerization |
| $h\nu$ | Radiation intensity for special initiation |
| $I_k$ | Initiator of type k |
| $M_j$ | Monomer of type j |
| $N_a$ | Number of chain transfer agents |
| $N_c$ | Number of coinitiators |
| $N_i$ | Number of initiators |
| $N_m$ | Number of monomers |
| $N_{rk}$ | Number of radicals (1 or 2) formed from the decomposition of initiator of type k |
| $N_s$ | Number of solvents |
| $N_x$ | Number of inhibitors |
| $P_n^i$ | Live polymer chain of length n having an active segment of type i |
| $R^\bullet$ | Primary radicals |
| $S_k$ | Solvent of type k (for solution polymerization) |
| $X_k$ | Inhibitor of type k |
| $\mu_0(j)$ | Zeroth moment of live polymer with respect to active segment of type j |
| $\mu_1(j)$ | First moment of live polymer with respect to segment j |
| $\lambda_0$ | Zeroth moment of bulk polymer (live + dead) |
| $\lambda_1(i)$ | First moment of bulk polymer (live + dead) with respect to segment i |
| $\lambda_2$ | Second moment of bulk polymer (live + dead) |

## Initiation

The initiation step involves the generation of reactive free-radicals followed by the addition of a monomer molecule (chain initiation) to form chain radicals of unit length ($P_1^i$). The non-chain or primary radicals ($R^\bullet$) may be generated by the thermal decomposition of a chemical initiator, a catalyzed initiation reaction involving electron transfer from ions, or by thermal/radiation induced mechanisms. Three types of initiation reactions are included in the built-in kinetics:

- Initiator decomposition reaction
- Induced initiation reaction
- Catalyzed initiation reaction

The initiator decomposition reaction accounts for primary radical generation from the thermal decomposition of chemical initiators.

The induced initiation reaction can be configured to account for the generation of radicals by thermal and radiation induced mechanisms from the monomers themselves, with or without the use of a coinitiator or promoter.

The catalyzed initiation reaction can be used to account for redox initiation, which has found wide application in aqueous emulsion polymerization systems.

The most commonly used radical generation method is the thermal decomposition of chemical initiators (usually peroxide or azo compounds) which decompose to form radicals when heated to an appropriate temperature. Only small amounts of the chemical initiator (less than 1 wt. % based on monomer) are needed. However, due to their high activation energies chemical initiators have a relatively narrow useful temperature range (approx. 30°C) over which the decomposition rates are neither too fast nor too slow.

*Initiator Decomposition Reaction*

The initiator decomposition reaction is modeled as a first order thermal decomposition reaction:

$$I_k \rightarrow N_{rk} R^\bullet \qquad R_{dk} = k_{dk} C_{Ik} \tag{4.2}$$

This rate expression ($R_{dk}$) describes the rate for the decomposition of initiator *k*. The rate expression for the formation of primary radicals from the decomposition of initiator *k* that are effective in initiating chain polymerization is given by:

$$R_{rk} = N_{rk} f_k k_{dk} C_{Ik} \tag{4.3}$$

There is a number of user specifiable parameters associated with this reaction. The user can specify more than one initiator to model systems where multiple initiators with different half-lives are used to control the initiation rate over the course of the polymerization. Depending on the initiator, either one or two primary radicals may be formed, hence the parameter $N_{rk}$ should be set to 1 or 2. Further, not all the initiator molecules that decompose will be effective in initiating chain polymerization. There can be significant radical recombination in the radical-cage leading to stable byproducts. An initiator efficiency $(f_k)$ has been added to the rate expression for this reason.

The rate constant $k_{dk}$ is calculated using a modified Arrhenius equation (Equation 4.1) with three parameters: pre-exponential factor, activation energy and activation volume. As noted previously, the activation volume accounts for the pressure dependence of the rate constant. This parameter is typically non-zero only at high pressures. Appendix G lists initiator decomposition rate constant parameters (pre-exponential factor and activation energies) for many commonly used initiators.

*Induced Initiation Reaction*

Free-radicals can also be generated from some monomers by thermal, radiative (UV, electron beam or gamma rays) or induced mechanisms. For example, styrene at temperatures above 120°C has a significant thermal initiation rate. The thermal initiation mechanism for styrene is believed to be 3rd-order in monomer (Hui and Hamielec, 1972). This reaction results in the formation of significant amounts of cyclic dimers and trimers which have to be removed during devolatilization. Hence, thermal initiation is not favored commercially. Radiation initiation has been used mainly for polymer modification to induce branching, crosslinking or grafting reactions. The induced initiation reaction, shown below, can be configured to model both these initiation mechanisms:

$$M_j + C_k \rightarrow P_1^j \qquad R_{si}^j = C_{Ck}^{aj} C_{Mj}^{bj} (h\nu)^{cj} \qquad \textbf{(4.4)}$$

For thermal initiation, the rate should be $R_{si} = k_{si} C_{Mj}^{bj}$ (set $a_j$, $c_j$ to zero).

For radiation initiation, the rate should be $R_{si} = k_{si} C_{Mj}^{bj} (h\nu)^{cj}$.

The induced initiation reaction can also account for the effects of using an initiator or promoter $(C_k)$ to increase the rate of radical generation.

*Catalyzed Initiation Reaction*

The catalyzed initiation reaction is similar to the initiator decomposition reaction except that a catalyst concentration term is included in the reaction rate expression:

$$I_k + C_j \rightarrow N_{rk} R^{\bullet} \qquad R_{ckj} = k_{ckj} C_{Ik} C_{Cj} \qquad \textbf{(4.5)}$$

This rate expression $(R_{ckj})$ describes the rate of consumption of initiator *k* and catalyst *j*. The corresponding rate expression for the formation of primary radicals that are effective in initiating chain polymerization is given by:

$$R_{rkj} = N_{rk} f_k k_{ckj} C_{Ik} C_{Cj} \qquad \textbf{(4.6)}$$

Any by-products that may be formed due to the catalyzed initiation reaction are currently not tracked.

To complete the initiation process, the reactive primary radicals $(R^{\bullet})$ react with monomer by the chain initiation reaction to form polymer chain radicals of unit length. The chain initiation reaction is shown below:

$$R^{\bullet} + M_j \rightarrow P_1^j \qquad R_{pi}^j = k_{pi}^j C_{Mj} R^{\bullet} \tag{4.7}$$

The chain radicals grow by successive addition of monomer molecules to form long chain polymer molecules.

## Propagation

The chain radicals grow or propagate by the addition of monomer molecules to form long polymer chains $(P_n^i)$. The propagation reaction is represented by:

$$P_n^i + M_j \rightarrow P_{n+1}^j \qquad R_p^{ij} = k_p^{ij} C_{Mj} P_n^i \tag{4.8}$$

where monomer *j* is being added to a polymer chain of length *n*, with an active segment of type *i*. The resulting polymer chain will be of length *n*+1 and the active segment will be of type *j*. The active segment type usually represents the last monomer incorporated into the polymer chain.

For copolymerization, there will be $N_m * N_m$ propagation reactions having different reactivities. For example, with two monomers, the monomer being added could be monomer 1 or monomer 2 while the active segment type could be segments from monomer 1 or monomer 2. Hence there will be four rate constants $(k_{11}, k_{12}, k_{21}, k_{22})$ where the first subscript refers to the active segment type while the second subscript refers to the propagating monomer type. For the terminal model the rate of propagation is dependent only on the active segment and propagating monomer concentrations.

This copolymerization scheme can be adapted for modeling the stereoregularity (isotactic, syndyotactic or atactic) and head-to-tail versus other modes (head-to-head, tail-to-tail) of monomer addition in homopolymerization.

## Chain Transfer to Small Molecules

Chain transfer to small molecules such as monomer, solvent or chain transfer agent usually involves the abstraction of hydrogen from the small molecule by the chain radical and leads to the termination of the live chain. At the same time, a new primary transfer radical is formed which can start chain polymerization. The effect of chain transfer on the polymerization kinetics depends on the reactivity of the transfer radical. When the transfer radical is very reactive, as is the case when the chain initiation rate constant is greater than the propagation rate constant, chain transfer will not lower the polymerization rate or conversion, but will reduce the molecular weight of the polymer. However, if the transfer radical is less reactive than the monomer-based propagating radical, as in the case of low chain initiation rate constant, both the conversion and molecular weight of the polymer will be lowered.

In the built-in kinetics chain transfer to monomer, transfer agent and solvent are included as shown below:

$$P_n^i + M_j \rightarrow D_n + P_1^j \qquad R_{trm}^{ij} = k_{trm}^{ij} C_{Mj} P_n^i \qquad \textbf{(4.9)}$$

$$P_n^i + A_k \rightarrow D_n + R^\bullet \qquad R_{tra}^{ij} = k_{tra}^{ij} C_{A_k} P_n^i \qquad \textbf{(4.10)}$$

$$P_n^i + S_k \rightarrow D_n + R^\bullet \qquad R_{trs}^{ij} = k_{trs}^{ij} C_{S_k} P_n^i \qquad \textbf{(4.11)}$$

For chain transfer to monomer a new chain radical of unit length is generated while for transfer to agent or solvent the transfer radicals are assumed to have the same reactivity as the primary radicals formed by initiation. The case where the transfer radical has a different reactivity than the primary radical will be added in a future version. The monomer transfer radical has a carbon-carbon double bond. Upon its chain propagation and termination a dead polymer chain with a terminal double bond is formed.

Chain transfer to polymer, which is also included in the kinetic scheme, is discussed in Long Chain Branching.

## Termination

Bimolecular termination of radicals may involve primary radicals ($R^\bullet$) and chain radicals ($P_n^j$). However, the concentration of primary radicals is usually much lower than the concentration of chain radicals. Hence, only bimolecular termination involving chain radicals is included in the built-in kinetic scheme. In termination, the chain radicals are destroyed and live chains are converted to dead polymer chains.

When the termination reaction leads to two dead chains the mechanism is termed disproportionation. Termination by combination leads to a single dead chain. Many monomers (e.g. MMA) show both types of termination while other monomers (e.g. styrene) terminate predominantly by combination:

$$P_n^i + P_m^j \rightarrow D_n + D_m \qquad R_{td}^{ij} = k_{td}^{ij} P_n^j P_n^i \tag{4.12}$$

$$P_n^i + P_m^j \rightarrow D_{n+m} \qquad R_{tc}^{ij} = k_{tc}^{ij} P_n^j P_n^i \tag{4.13}$$

The mode of termination will have a strong influence on the average polymer chain length and chain length distribution especially when chain transfer is not significant. Further, these termination reactions form special groups in the dead polymer chains which effect some polymer properties. Disproportionation results in one of the dead chains having a saturated end-group while the other will have an end-group with a terminal double bond. Combination results in a head-to-head sequence near the middle of the chain. Head-to-head sequences and double bond end-groups can contribute to thermal instability and may cause degradation, branching and gelation during storage or subsequent processing.

Inhibition is included as an additional termination mechanism. This involves reaction between a chain radical and a small molecule (inhibitor or impurities) to form a dead chain:

$$P_n^i + X_k \rightarrow D_n \qquad R_x^{ik} = k_x^{ik} C_{X_k} P_n^i \tag{4.14}$$

*Termination Between Chain Radicals*

Bimolecular termination reactions between chain radicals become diffusion controlled at high polymer concentration or high conversion. This leads to an increase in the polymerization rate and molecular weight. This condition is known as the *gel effect* or Trommsdorff effect. At high conversions the increased viscosity of the reaction medium imposes a diffusional limitation on the polymer chains, leading to lower effective termination rates. Eventually at high enough conversions, even the propagation, initiation, and chain transfer rates may be affected by the diffusional limitation.

The diffusional limitation is modeled by multiplying the low conversion reaction rate coefficients by a gel-effect factor that will lower their effective value with increasing conversion. Several correlations are included for the gel-effect factor that relate it to the reactor conversion and operating conditions.

## Short and Long Chain Branching

There are two types of branching reactions in the kinetic scheme:

- Chain transfer to polymer, which leads to long-chain branches
- Backbiting or intramolecular radical transfer reactions resulting in short-chain branches

The backbiting reaction is described in Beta-Scission. Radical backbiting followed by propagation of the backbone radical leads to short chain branching:

$$P_n^i \rightarrow P_n^j \qquad R_{scb}^{ij} = k_{scb}^{ij} P_n^i \tag{4.15}$$

Long chain branching can be due to chain transfer to polymer or due to reactions involving a live chain and a terminal or internal double bond on another polymer chain. Internal double bonds are built into the polymer chain when one of the propagating monomers is a diene or when vinyl and divinyl moments are copolymerized. Polymer chains with terminal double bonds are formed by chain transfer to monomer, termination by disproportionation, and beta-scission reactions or beta-hydride elimination. Only the chain transfer to polymer reaction is included in the built-in kinetics. It is further assumed that the transfer is to a dead polymer chain. This assumption is reasonable because the concentration of live chains is usually much less than the concentration of dead chains:

$$P_n^i + D_m \rightarrow D_n + P_m^j \qquad R_{trp}^{ij} = k_{trp}^{ij} m_j D_m P_n^i \qquad \textbf{(4.16)}$$

## Beta-Scission

The polymer radical can experience backbiting or intramolecular radical transfer reactions where the radical at the chain end gets transferred to a hydrogen atom attached to the chain carbon five or six carbon atoms from the chain end. Hence, a fraction of the live polymer molecules have active centers located on the backbone while the remainder have active centers located on the chain ends. The backbiting reaction leads to short chain branches if the backbone radicals are stable and can continue propagation.

However, for some polymers (e.g. polypropylene) the backbone radical can be highly unstable and will result in the scission of the chain into a dead polymer chain with a terminal double bond and a short live chain one to six carbon atoms long. The beta-scission reaction could also result in a short dead chain and a long live chain.

A simplified beta-scission reaction is included in the built-in kinetics. It is limited to reactions where a live chain undergoes scission to form a dead chain of the same length and a primary radical:

$$P_n^i \rightarrow D_n + R^{\bullet} \qquad R_{sc}^i = k_{sc}^i P_n^i \qquad \textbf{(4.17)}$$

# MODEL FEATURES AND ASSUMPTIONS

Following are the model features and assumptions used in the free-radical polymerization model available in Polymers Plus.

## Calculation Method

In the Polymers Plus Free-radical bulk/solution polymerization model, the polymer chain length distribution averages and molecular structure properties are calculated using the population balance and method of moments approach, based on the built-in kinetics in Figure 4.6. Population balance equations are used to account for the concentration of live polymer chains and combined polymer chains of length *n*. The *f*-th live and combined polymer chain length distribution moments are defined as follows:

$$\mu_{\underline{f}}^{j} = \sum_{\underline{n}=0}^{\infty} \underline{n}^{\underline{f}} P_{\underline{n}}^{j} \qquad \textbf{(4.18)}$$

$$\lambda_{\underline{f}} = \sum_{\underline{n}=0}^{\infty} \underline{n}^{\underline{f}} \left( \sum_{j=1}^{N_m} P_{\underline{n}}^{j} + D_{\underline{n}} \right) \qquad \textbf{(4.19)}$$

For homopolymerization the index *f* is a scalar variable and the active segment superscript *j* may be dropped for the live polymer moment definition as there is only one segment type. Hence, for homopolymerization there will be one zeroth moment, one first moment, one second moment and so on for the live and combined polymer. However, for copolymerization, the index *f* will be a vector whose elements denote the monomer with respect to which the moment is defined. For copolymerization with respect to every active segment, there will be one zeroth moment, $N_m$ first moments, $N_m + \frac{N_m(N_m\text{-}1)}{2}$ second moments and so on.

For example, for copolymerization with three monomers, the vector index *f* can have the following values for the first moment:

$$\underline{f} = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \quad \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, \quad \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$

representing the first moment with respect to segment one, two and three respectively. The application of the moment definitions to the live and bulk polymer population balance equations yields the live and bulk polymer chain length distribution moment equations. The general moment equations are listed in Figure 4.7 and Figure 4.8. The various zeroth, first, second, etc. moment equations can be generated from these by substituting the appropriate values for the index *f*.

## Quasi-Steady-State Approximation (QSSA)

Users may invoke the Quasi-Steady-State Approximation (QSSA) for the live moment equations. Invoking QSSA converts the live moment differential equations (ODE) to algebraic equations which are solved internally in the kinetics routine. Assuming QSSA is equivalent to assuming that the live moments attain their steady-state values instantaneously. This approximation makes the system of ODE's much easier to integrate by reducing stiffness.

Comparison of the results with and without QSSA for most free-radical polymerization systems, where the chain lifetimes are short compared to the residence time, show negligible differences. Therefore it is usually reasonable to use the QSSA. However, users should check the validity of this approximation by running cases with the QSSA switch set to YES and NO for their particular system. By default the QSSA is turned off (QSSA switch is set to NO). Users have the option of invoking the QSSA for all the live polymer moment equations, or selectively for only the zeroth, first, or second moment of live polymer.

## Phase Equilibrium

The polymerization model can currently consider either a single phase system (vapor or liquid) or a two phase system (vapor and liquid) in calculating concentrations for the reaction kinetics. For single phase systems, the reacting phase may be either vapor or liquid. For two phase systems, the liquid phase is assumed to be the reacting phase, and all the polymer is assumed to be in the liquid phase. The phase equilibrium model will be extended in the future to include vapor-liquid-liquid phase equilibrium (VLLE).

## Gel Effect

Bimolecular termination reactions between chain radicals become diffusion controlled at high polymer concentrations or high conversion leading to an initial increase in the polymerization rate and molecular weight. This condition is known as the *gel effect* or Trommsdorff effect. At high polymer concentrations, the increased viscosity of the reaction medium imposes a diffusional limitation on the polymer chains which leads to lower effective termination rates. Typically the termination rate coefficients are affected first by the gel effect because they involve diffusion of two bulky polymer radicals. Eventually at high enough conversions, even the propagation, initiation, chain transfer reactions, and the initiator efficiency are lowered by the gel effect. Hence, in general it may be necessary to allow gel effects for all the polymerization reactions in the built-in kinetic scheme.

*Diffusional Limitation*

The diffusional limitation is usually modeled by multiplying the low conversion reaction rate coefficients, $k_o$, by a gel effect factor, *GF*, that decreases with increasing conversion. Hence the effective rate coefficient for a reaction is given by:

$$k_{eff} = k_o GF$$

Several empirical and semi-empirical correlations are available in the literature which relate the gel effect factor to reactor conversion and operating conditions. Currently two of these have been implemented as built-in correlations. Users will be able to use these gel effect correlations simply by specifying the correlation number and the parameters. The built-in correlations are:

Correlation Number 1:

$$GF = \frac{a_1}{1 + a_2 X_p^{a_3}} \qquad \textbf{(4.20)}$$

Where:

$X_p$ = weight fraction of polymer

This correlation has three user specified parameters, $a_1$, $a_2$, and $a_3$.

Correlation Number 2:

$$GF = \left( \frac{A}{1 - a_9 X_p} \exp\left[ -\left( BX_p + CX_p^2 + DX_p^3 \right) \right] \right)^{a_{10}} \qquad \textbf{(4.21)}$$

With:

$A = a_1 + a_2 T$

$B = a_3 + a_4 T$

$C = a_5 + a_6 T$

$D = a_7 + a_8 T$

Where:

$X_p$ = weight fraction of polymer

$T$ = temperature in Kelvin

This correlation has ten user specified parameters, $a_1$ to $a_{10}$.

Users may also include their own gel effect correlation by specifying a correlation number greater than the number of built-in gel effect correlations (currently two). In this case, users must provide the correlation for the gel effect factor in the form of a Fortran subroutine. The argument list is documented in Table 4.42.

## *Table 4.42 User Gel Effect Subroutine Arguments*

### User Subroutine Arguments

```
Subroutine USRGEL ( ICORR, MAXGP , GPAR ,WFTFRP , GF,
+              SOUT  ,NSUBS ,IDXSUB,ITYPE ,
+              NINTK ,INTK  ,NREALK,REALK ,
+              NPO   ,NBOPST,IDS   ,NCK   ,
+              NITG  ,ITG   ,NREA  ,REA   )
```

### Argument Descriptions

| Variable | I/O | Type-Spec | Dimension | Description |
|---|---|---|---|---|
| ICORR | I | I | | Gel effect correlation number |
| MAXGP | I | I | | Maximum number of gel effect parameters |
| GPAR | I | R | MAXGP | Gel effect parameters |
| WTFRP | I | R | | Weight fraction of polymer |
| GF | O | R | | Gel effect factor |
| SOUT | I | R | | Outlet stream |
| NSUBS | I | I | | Number of substreams |
| IDXSUB | I | I | NSUBS | Location of substreams in stream vector |
| ITYPE | I | I | NSUBS | Substream type vector<br>1 = MIXED<br>2 = CISOLID<br>3 = NC |
| NINTK | I | I | | Number of integers for model |
| INTK | I/O | I | NINT | Integer array for model |
| NREALK | I | I | | Number of reals for model |
| REALK | I/O | R | NREAL | Real array for model |
| NPO | I | I | | Number of property methods |
| NBOPST | I | I | 6, NPO | Property method array |
| IDS | I | I | 2, 13 | Block IDs<br>i, 1 Block ID<br>i, 2 to i, 4 used by system<br>i, 5 kinetic subroutine name |
| NCK | I | I | | Total number of components |
| NITG | I | I | | Length of integer array for kinetics |
| ITG | I | I | NITG | Integer array for kinetics |
| NREA | I | I | | Length of real array for kinetics |
| REA | I | R | NREA | Real array for kinetics |

# POLYMER PROPERTIES CALCULATED

The following variables can be calculated by the built-in kinetics routine based on the polymer attributes and the subset of the built-in kinetics used for a specific simulation:

- Zeroth, first and second moments for the combined polymer
- Zeroth and first moments for the live polymer
- Number, weight and z-average degree of polymerization and polydispersity index for the combined polymer (DPN, DPW, DPZ, PDI)
- Number, weight and z-average molecular weight for the combined polymer (MWN, MWW, MWZ)
- Average molecular weight of segments in combined polymer (MWSEG)
- Copolymer segment composition for combined polymer (SFLOW, SFRAC)
- Total number of short and long chain branches (SCB, LCB)
- Short and long chain branching frequencies (FSCB, FLCB)
- Mole fraction of combined polymer chains that are live (LDFRAC)
- Number average degree of polymerization for live polymer (LDPN)
- Copolymer segment composition for live polymer (LSFLOW, LSFRAC)
- Live polymer active segment composition (LEFLOW, LEFRAC)

These parameters are stored as component attributes defined in Chapter 2.

These variables, except for the branching frequencies, are related to the moments by the relationship in Figure 4.9. The branching frequencies are calculated from the rate of chain transfer to polymer and the rate of backbiting reactions. The branching frequencies are reported in terms of number of branches per thousand monomer molecules in the polymer.

*Structural Properties*

Frequently some of the polymer properties are reported in terms of other properties that are related to these structural properties. These include properties such as melt flow rate or melt index, viscosity numbers, or K-values, etc. User-property subroutines can be set up for calculating some of these polymer properties from the polymer moments and structural properties.

*User Profile Properties*

In addition to the polymer properties reported through the component attributes, additional results are reported through *User Profile* variables. The following user profile variables are currently hard-wired in the built-in kinetics routine:

- Conversion of monomer to polymer (Fraction)
- Rate of polymerization (propagation) (KMOL/S/CUM)
- Heat of polymerization (KCAL/S/CUM)
- Reacting phase volume (or volume flow) (CUM or CUM/S)
- Reacting phase total moles (or mole flow) (KMOL or KMOL/S)
- Reacting phase average molecular weight (KG/KMOL)
- Rate of chain termination by combination (KMOL/S/CUM)
- Rate of chain termination by disproportionation (KMOL/S/CUM)

- Rate of chain termination by inhibition (KMOL/S/CUM)
- Rate of initiation of radicals (KMOL/S/CUM)
- Rate of induced initiation (KMOL/S/CUM)
- Rate of chain transfer to monomers (KMOL/S/CUM)
- Rate of chain transfer to polymer (KMOL/S/CUM)
- Rate of chain transfer to agents (KMOL/S/CUM)
- Rate of chain transfer to solvents (KMOL/S/CUM)
- Rate of beta scission (KMOL/S/CUM)
- Rate of short chain branching (KMOL/S/CUM)
- Concentration of initiators (KMOL/CUM)
- Concentration of catalysts (KMOL/CUM)
- Concentration of coinitiators (KMOL/CUM)
- Concentration of monomers (KMOL/CUM)
- Concentration of transfer agents (KMOL/CUM)
- Concentration of solvents (KMOL/CUM)
- Concentration of inhibitors (KMOL/CUM)
- Concentration of polymer (KMOL/CUM)

*Rates and Concentrations*

The rates and concentrations reported via the user profiles can be used to calculate additional information, such as the kinetic chain length and fraction of dead chains with terminal double bond segments. These user profile variables can only be accessed if you are calling the free-radical kinetics from a batch reactor (RBATCH) or a plug flow reactor (RPLUG).

$$\frac{d\mu_{\underline{f}}^{j}}{dt} = \left[\delta\left(\underline{n} - \underline{\delta} j\right)\right]^{\underline{f}} \left( k_{pi}^{j} C_{Mj} R^{\bullet} + \sum_{i=1}^{N_m} k_{trm}^{ij} C_{Mj} \mu_0^i + k_{si}^{j} C_C^{aj} C_{Mj}^{bj} (h\nu)^{cj} \right)$$

$$+ \sum_{i=1}^{N_m} k_p^{ij} C_{Mj} \sum_{\underline{a}=\underline{0}}^{\underline{f}} \left( \frac{\underline{f}}{\underline{a}} \right) \left(\underline{\delta} j\right)^{\left(\underline{f}-\underline{a}\right)} - \sum_{i=1}^{N_m} k_p^{ji} C_{Mi} \mu_{\underline{f}}^{j}$$

$$- \alpha^j \mu_{\underline{f}}^{j} + \sum_{i=1}^{N_m} k_{trp}^{ij} \lambda_{\underline{f}+\underline{\delta} j} \mu_{\underline{0}}^{i}$$

$$- \sum_{i=1}^{N_m} k_{scb}^{ji} \mu_{\underline{f}}^{j} + \sum_{i=1}^{N_m} k_{scb}^{ij} \mu_{\underline{f}}^{i}$$

$$- \sum_{i=1}^{N_m} \left( k_{td}^{ij} + k_{tc}^{ij} \right) \mu_{\underline{0}}^{i} \mu_{\underline{f}}^{j}$$

where $\alpha^j$ contains some terms for reactions leading to the formation of dead polymer

$$\alpha^j = \left( \sum \underline{m}_{i=1}^{N_m} k_{trm}^{ji} C_{Mi} + \sum_{i=1}^{N_m} k_{trp}^{ji} \lambda_1(i) + \sum_{k=1}^{N_a} k_{tra}^{jk} C_{Ak} + \sum_{k=1}^{N_s} k_{trs}^{jk} C_{Sk} + k_{sc}^{j} + k_{k,x}^{j} C_{Xk} \right)$$

***Figure 4.7*** *Live Polymer Chain Length Distribution Moment Equation*

$$\frac{d\lambda_{\underline{f}}}{dt} = \sum_{j=1}^{N_m}\left[\delta\left(\underline{n}-\underline{\delta}j\right)\right]^{\underline{f}}\left(k_{pi}^{j}C_{Mj}R^{\bullet} + \sum_{i=1}^{N_m}k_{trm}^{ij}C_{Mj}\mu_0^i + k_{si}^{j}C_C^{aj}C_{Mj}^{bj}\left(h\nu\right)^{cj}\right)$$

$$+\sum_{j=1}^{N_m}k_p^{ij}C_{Mj}\sum_{\underline{a}=\underline{0}}^{f}\left(\frac{f}{\underline{a}}\right)\left(\underline{\delta}j\right)^{\left(\underline{f}-\underline{a}\right)}\mu_{\underline{a}}^{i} - \sum_{i=1}^{N_m}k_p^{ji}C_{Mi}\mu_{\underline{f}}^{j}$$

$$-\sum_{i=1}^{N_m}\sum_{j=1}^{N_m}k_{tc}^{ij}\mu_{\underline{0}}^{i}\mu_{\underline{f}}^{j} + \frac{1}{2}\sum_{i=1}^{N_m}\sum_{\underline{a}=\underline{0}}^{\underline{f}}\left(\frac{f}{\underline{a}}\right)k_{tc}^{ij}\mu_{\underline{a}}^{i}\mu_{\underline{f}-\underline{a}}^{j}$$

***Figure 4.8*** *Bulk Polymer Chain Length Distribution Moment Equation*

$$DPN = \frac{\sum_{i=1}^{N_m}\lambda_1(i)}{\lambda_0}$$

$$LDPN = \frac{\sum_{i=1}^{N_m}\mu_1(i)}{\sum_{i=1}^{N_m}\mu_0(j)}$$

$$SFRAC(I) = \frac{\lambda_1(i)}{\sum_{i=1}^{N_m}\lambda_1(i)}$$

$$LSFRAC(I) = \frac{\mu_1(i)}{\sum_{i=1}^{N_m}\mu_1(i)}$$

$$PDI = \frac{\lambda_2\lambda_0}{\left(\sum_{i=1}^{N_m}\lambda_i(1)\right)^2}$$

$$LPFRAC = \frac{\sum_{j=1}^{N_m}\mu_0(j)}{\lambda_0}$$

$$LEFRAC(I) = \frac{\mu_0(j)}{\sum_{j=1}^{N_m}\mu_0(j)}$$

***Figure 4.9*** *Relationship Between Moments and Polymer Properties*

# SPECIFYING FREE-RADICAL POLYMERIZATION KINETICS

## Accessing the Free-Radical Model

To access the Free-Radical polymerization kinetic model:

1. From the Data Browser, find the **Reactions** folder.
2. From the **Reactions** folder, select **Reactions** again to get to the Reactions object manager.

   If the kinetic model already exists, double-click on the desired Reaction ID in the object manager or select **Edit** to get to the input forms.
3. To add a new model, from the **Reactions** object manager, select **New**. If necessary, change the default ID for the reaction.
4. Select Free-Rad as the reaction type and click on **OK**.

## Specifying the Free-Radical Model

The Free-Radical model input forms are listed below:

| Use this sheet | To |
|---|---|
| Species | Define reacting species |
| Reactions | Specify reactions and rate constant parameters |
| Rate Constants | Summarize rate constant parameters |
| Options | Select additional options |
| Gel Effect | Supply gel-effect correlation parameters |

## Specifying Reacting Species

You must specify the reacting species in the **Species** sheet:

1. In the **Polymer** field, specify the polymer produced.
2. In the **Monomers** field list the reacting monomers. For each monomer, in the **goes to** → field specify the polymer segment which the monomer converts to.
3. Continue listing other types of reacting species, e.g. solvents, transfer agents, etc.
4. Select the **Generate Reactions** option if you would like the reactions to be generated automatically.

   After going through the reaction generation once, it is recommended that you turn off this feature. Otherwise, the reaction generation will be performed repeatedly.

## Listing Reactions

The Free-Radical model generates reactions based on the list of reacting species. You can view the system-generated reactions, then assign rate constant parameters to these reactions.

You can view a list of the system-generated reactions on the Reactions sheet. In the Reaction summary listing, for each reaction the first column indicates the reaction type. The second column lists the reactants, and the last column lists the products. The Data Browser window can be resized to better view the reaction listing. Use the following options:

| Click on | To |
|---|---|
| New | Add new reactions to the scheme |
| Edit | Edit the current reaction indicated by the row selector |
| Rate Constants | Specify reaction rate constant parameters for the reactions |

Click to select a reaction. Click a reaction then Control-Click to include additional reactions for multiple selection. Double-click to edit a reaction.

In addition, you may use the following buttons:

| Click on | To |
|---|---|
| Hide/Reveal  | Exclude/Include a reaction from the calculations |
| Delete  | Permanently remove a reaction from the model |

## Adding Reactions

To add a new reaction to the scheme click **New** to open the Add Reaction subform:

1. In **Reaction type**, select a type for the new reaction. The **Reaction scheme** for that type is displayed.
2. In other reactant (e.g. **Initiator**, **Catalyst**) fields enter the reactants of the categories allowed for that reaction type.
3. Click on **Cancel** to discard the new reaction

   – or –

   Click on **New** to add a new reaction

   – or –

   Click on  to check the **Completion status**

   – or –

   Click on **Done** to return to the reaction summary.

## Editing Reactions

To edit a reaction, click on **Edit** to open the Edit Reaction subform. When you open the Edit Reaction subform:

1. Modify the **Reaction type** as needed. The **Reaction scheme** for that type is displayed.
2. Modify reactants as needed.
3. Click on  to check the **Completion status**

   – or –

   Click on **Done** to return to the reaction summary.

## Assigning Rate Constants to Reactions

To assign rate constants to user reactions, click on **Rate Constants** to open the Rate Constant Parameters subform:

1. In the **ko** field, enter the pre-exponential factor.
2. In the **Ea** field, enter the activation energy.
3. In the $\Delta$**V** field, enter activation volume.
4. In the **Tref** field, enter reference temperature.
5. In the **Efficiency** field, enter initiator efficiency for initiation reactions.
6. In the **No. radicals** field, enter the number of primary radicals formed in initiation reactions.
7. Click on the stoichiometry list and select a new reaction to enter rate constants for another reaction. You can use the **Prev** and **Next** buttons to select the previous or next reaction in the list.
8. Click on the Summary tab to see a listing of all the rate constant parameters.
9. Click on  to check the **Completion status**

   – or –

   Click on **Close** to return to the reaction summary.

## Selecting Calculation Options

You can select additional simulation options for the model such as QSSA, special initiation options, and gel-effect on the Options tab sheet.

For QSSA, select the moments for which you would like this option.

For special initiation, specify the monomers affected, then enter the special initiation coefficients.

For Gel effect, you need to specify parameters on the **Gel Effect** sheet.

## Adding Gel-Effect

Use the Gel-Effect sheet to add gel effect to reactions:

1. Enter a unique integer identifier in **No**.
2. In the **Reaction** field, specify the reaction to which you would like to apply gel effect.
3. In the **Corr. No.** field, specify a gel effect correlation number.
4. In **Parameters**, list the parameters for the gel effect correlation.

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# 4.3 EMULSION POLYMERIZATION MODEL

This section covers the emulsion polymerization model available in Polymers Plus.

Topics covered include:

- Summary of Applications
- Emulsion Polymerization Processes
- Reaction Kinetic Scheme
- Model Features and Assumptions
- Polymer Particle Properties Calculated
- Specifying Emulsion Polymerization Kinetics

The *Polymers Plus Examples & Applications Case Book* illustrates how to use the emulsion model to simulate styrene butadiene copolymerization.

# SUMMARY OF APPLICATIONS

The emulsion polymerization model is applicable to emulsion polymerization processes where nucleation occurs by both the micellar and homogeneous mechanisms. Some of the applicable polymers are described below:

- Styrene - A component of synthetic rubber and paper coating
- Butadiene - Synthetic rubber, impact modifier in ABS and HIPS
- Tetrafluroethylene - Polytetrafluroethylene (PTFE), fluoropolymers Viton
- Vinylacetate - Polyvinylacetate (PVA) adhesives, paint formulation
- Methylmethacrylate - Surface coating applications.
- Acrylic Acid - Minor component in paints
- 2-chloro-1,3-butadiene (chloroprene) - Neoprene rubber
- Butyl Acrylate - Surface coatings
- Butyl Methacrylate - Comonomer in surface coatings
- Vinyl Chloride - PVC used in floor covering and coatings

A wide variety of processes are used in emulsion polymerization. The processes which can be modeled using the Polymers Plus emulsion polymerization model are those that follow micellar, homogeneous or seeded polymerization.

An example of a process that follows micellar nucleation and subsequent growth is the production of SBR latex in semi-batch reactors for paper coating applications. The following lists polymeric products made by emulsion polymerization:

- Emulsion paints, made from a number of monomers (styrene, butadiene, acrylates, etc.) and a variety of other ingredients
- Adhesives, from slightly plasticized poly(vinyl acetate) and poly(ethylene-co-vinyl acetate) - a pressure sensitive adhesive
- SBR, for carpet backing and for coating paper and card board along with china clay, thus facilitating printing on surfaces
- Non-woven fabrics, which have their fabrics pre-coated with polymer and then heat pressed (these are termed “thermoformable” felts)
- ABS (Acrylonitrile-Butadiene-Styrene), used in high impact strength material made by swelling of a polybutadiene latex with a mixture of styrene and acrylonitrile and polymerizing further. HIPS (High-Impact PolyStyrene) made from bulk polymerized polystyrene in the presence of polybutadiene

# EMULSION POLYMERIZATION PROCESSES

Emulsion polymerization is an industrially important process for the production of polymers used as synthetic rubber, adhesives, paints, inks, coatings, etc. The polymerization is usually carried out using water as the dispersion medium. This makes emulsion polymerization less detrimental to the environment than other processes in which volatile organic liquids are used as a medium.

In addition, emulsion polymerization offers distinct processing advantages for the production of polymers. Unlike in bulk or solution polymerization, the viscosity of the reaction mixture does not increase as dramatically as polymerization progresses. For this reason, the emulsion polymerization process offers excellent heat transfer and good temperature throughout the course of polymer synthesis. This process is always chosen when the polymer product is used in latex form.

# REACTION KINETIC SCHEME

In emulsion polymerization, free-radical propagation reactions take place in particles isolated from each other by the intervening dispersion medium. This reduces termination rates, giving high polymerization rates, and simultaneously makes it possible to produce high molecular weight polymers. One can increase the rate of polymerization without reducing the molecular weight of the polymer. Emulsion polymerization has more recently become important for the production of a wide variety of specialty polymers.

*Particle Formation*

To appreciate the complexities of emulsion polymerization, a basic understanding of the fundamentals of particle formation and of the kinetics of the subsequent particle growth stage is required. A number of mechanisms have been proposed for particle formation. It is generally accepted that any one of the mechanisms could be responsible for particle formation depending on the nature of the monomer and the amount of emulsifier used in the recipe.

The two common mechanisms for particle formation are:

- Micellar nucleation
- Homogeneous nucleation

With *micellar nucleation*, micelles, which are aggregates of emulsifier molecules, act as the site of nucleation.

With *homogeneous nucleation*, the radicals produced in the aqueous phase polymerize with dissolved monomer and precipitate out to form precursor particles. The precipitated precursor particles coagulate with each other until a stable particle is formed.

## Micellar Nucleation

Micellar nucleation is considered to be the primary mechanism for particle formation (Harkins, 1945; Smith & Ewart, 1948) in those emulsion polymerization systems for which the monomer is very sparingly soluble in water, and where the concentration of emulsifier is above the *critical micelle concentration* (CMC). As the name implies, the micelles, which are formed when the emulsifier concentration is above the CMC, act as the site for particle nucleation.

The reaction mixture consists of water, monomer, emulsifier and a water-soluble initiator. The monomer is dispersed in the form of droplets in the water by agitation. The droplets formed are stabilized by the emulsifier molecules which are adsorbed on the droplet surface. In addition to the droplets, monomer is also found dissolved in the aqueous medium and solubilized inside the micelles.

Similarly, the emulsifier is found in three locations: in the micelles, dissolved in the aqueous medium, and adsorbed on the monomer droplets. Since a water soluble initiator is used, the initiator molecules will be mainly found dissolved in the water medium.

When a typical emulsion polymerization recipe is heated, the initiator dissociates in the aqueous medium and produces initiator radicals. Upon propagating with monomer in the water phase the initiator radicals form oligomeric radicals and enter the micelles, which are aggregates of emulsifier molecules inside which a small amount of monomer is entrapped. The capturing of a radical by micelle and reaction with the entrapped monomer signifies the formation of a particle from a micelle. As the propagation takes place in the newly created particle, a thermodynamic potential difference is created for the diffusion of the monomer from the monomer droplets into the growing particles.

As the particles grow, some of the micelles disintegrate and cover the growing particles to stabilize them. Therefore, the micelles are not only consumed in the formation of polymer particles, but also in the stabilization of growing polymeric particles. In fact, approximately one percent of the micelles are used in the formation of particles. When no micelles remain in the reaction mixture, micellar nucleation ceases.

*Stage I*

The time required for particle nucleation to be complete is also called the *nucleation time* or the *nucleation period*, and usually lasts 10-15 minutes in conventional polymerization systems. This is commonly referred to as the *seed stage*, or Stage I, in the emulsion polymerization industry. After the nucleation or seed stage, the number of particles in the reaction mixture remains constant if particles do not agglomerate.

*Stage II*

The stage following the seed stage is called the *growth stage* or Stage II of the emulsion polymerization. In Stage II, the polymer particles grow through a steady diffusion of monomer from the monomer droplets to the particles. Since the number of particles remains constant and the particles are saturated with monomer, this stage is marked by a constant rate of polymerization and could easily be observed on a conversion vs. time plot. Stage II is considered complete when the monomer droplets are totally depleted.

*Stage III*

In Stage III, the monomer finishing stage, the reaction mixture consists of the monomer swollen polymer particles and the aqueous medium. Further polymerization of the monomer in the particles takes place. This results in a decrease of the particle size due to higher density of the polymer compared to the monomer. During Stage III, the concentration of monomer dissolved in the aqueous phase falls rapidly, as does the concentration in the polymer particles. The final product obtained at the end of Stage III is called *latex*.

Figure 4.10 illustrates the stages in emulsion polymerization reaction.

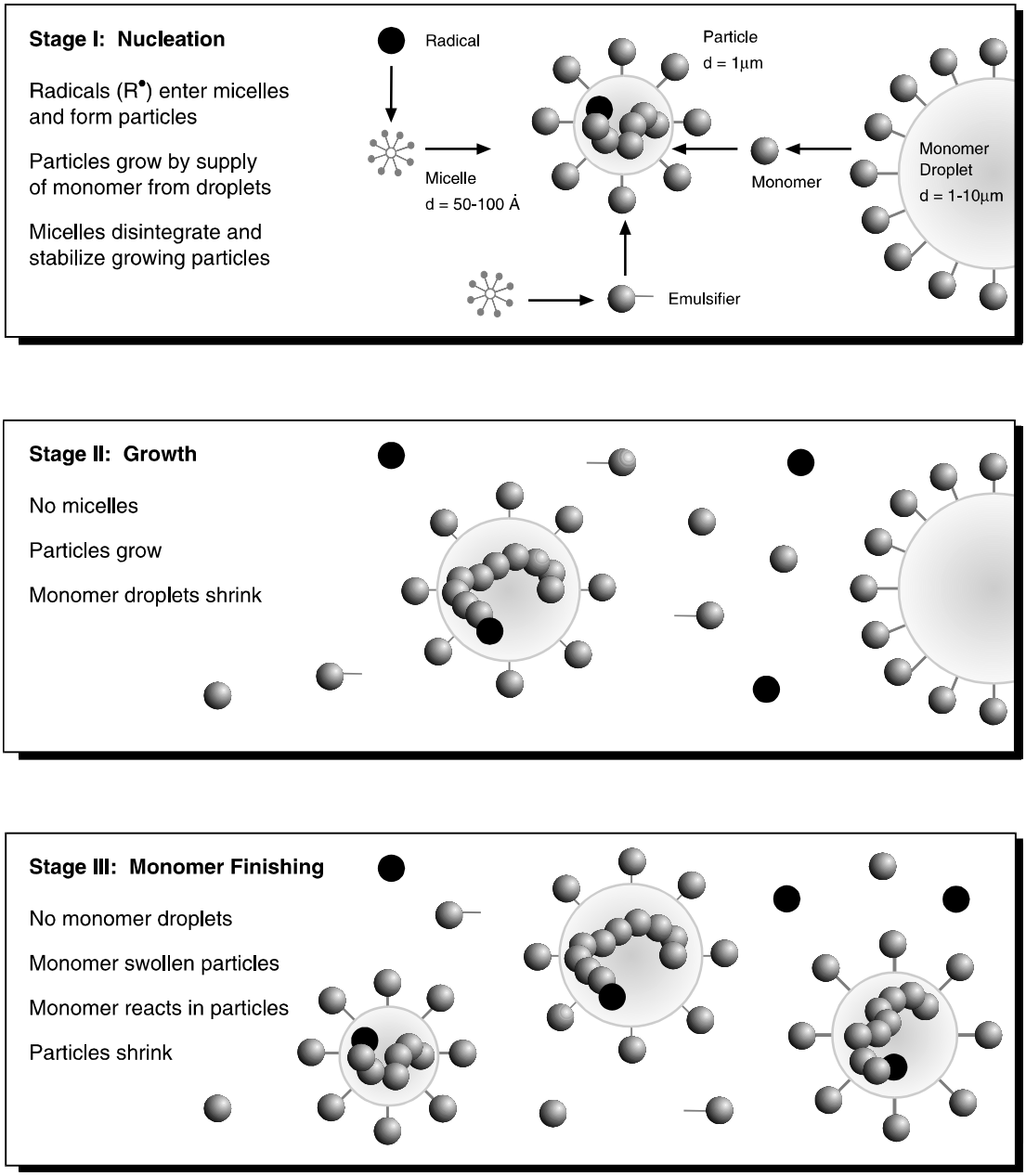


***Figure 4.10*** *Micellar Nucleation Emulsion Polymerization Stages*

*Particle Number and Nucleation Time*

The number of particles, usually in the range of $10^{16}$ to $10^{18}$ per liter of latex, is an important parameter in emulsion polymerization. Smith and Ewart have derived mathematical expressions for the number of particles under the following assumptions (Smith and Ewart, 1945):

1. Particles as well as micelles are equally effective in capturing radicals from the aqueous phase
2. Temperature of the reaction is constant
3. Volumetric growth rate of polymer particles is constant

With these assumptions, the particle number and nucleation time are given by the following equations:

$$N_p = 0.37\left(\frac{R_I N_a}{\dot{v}}\right)^{0.4}\left(A_s E\right)^{0.6} \quad \textbf{(4.22)}$$

$$t_{nuc} = 0.65\left(\frac{1}{\dot{v}}\right)^{0.4}\left(\frac{A_s E}{R_I N_a}\right)^{0.6} \quad \textbf{(4.23)}$$

$R_I N_a$ is the rate of generation of radicals in the water phase, and $\dot{v}_s$ is the volumetric growth rate of swollen polymer particles. They are determined from the following equations:

$$R_I = 2 f k_d I \quad \textbf{(4.24)}$$

$$\dot{v}_s = \frac{k_p M_p \bar{n}}{N_a}\frac{MW_m}{d_p}\frac{1}{\varphi_p} \quad \textbf{(4.25)}$$

Where:

| | | |
|---|---|---|
| $f$ | = | initiator efficiency |
| $k_d$ | = | rate constant for initiator dissociation |
| $I$ | = | initiator concentration |
| $N_a$ | = | Avogadro's number |
| $k_p$ | = | propagation constant |
| $M_p$ | = | monomer concentration inside the particles |
| $\bar{n}$ | = | average number of radicals per particle |
| $MW_m$ | = | molecular weight of the monomer |
| $d_p$ | = | density of polymer |
| $\varphi_p$ | = | volume fraction of polymer in the particle phase |

## Homogeneous Nucleation

Homogeneous nucleation is the mechanism for particle formation when monomers are more water soluble and level of emulsifier is not high enough for the formation of micelles in the recipe.

Figure 4.11 shows a detailed picture of kinetic events that take place during particle formation by homogeneous nucleation.

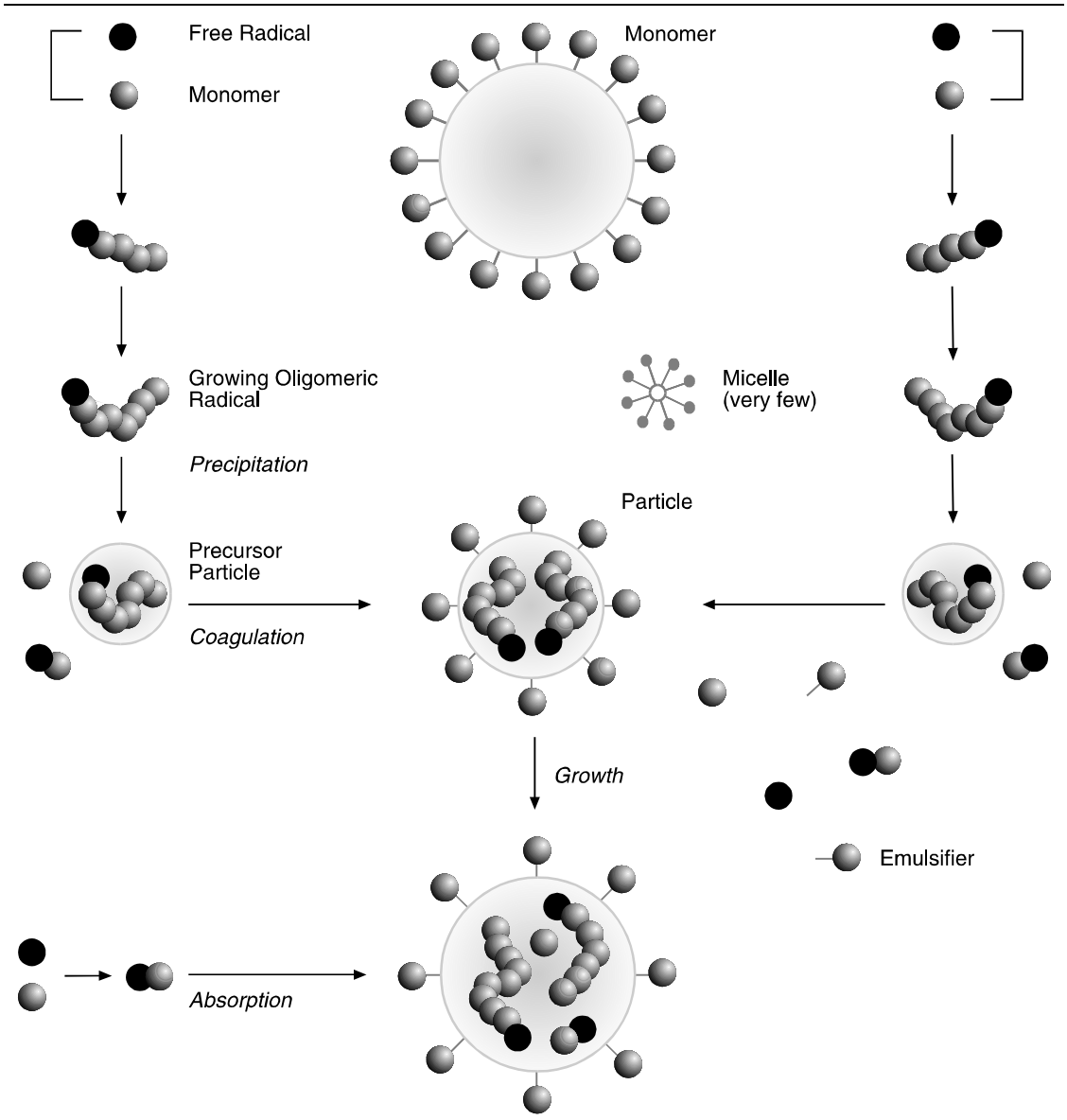


***Figure 4.11*** *Homogeneous Nucleation*

When the reaction mixture is heated the initiator molecules dissolved in the water medium dissociate and produce the initiator radicals. These initiator radicals react with the dissolved monomer and quickly propagate into an oligomeric radical in the water phase.

As the size of the oligomeric radical increases it becomes insoluble in water and precipitates out of the water phase. This event signifies the formation of a primary polymer particle from the growing oligomeric radical in the water phase. However, these primary particles are not stable, and, hence, coagulate with each other until enough surface charge is developed to stabilize the particles. These surface charges are provided by the ionic end of the initiator molecules. In addition, the coagulated particles are also stabilized by ionic and non-ionic emulsifier added to the emulsion recipe.

Once a stabilized particle is formed, it grows by getting a steady supply of monomer from monomer droplets by diffusion. As the particles grow and become large, the oligomeric radicals that are formed in the water phase are directly absorbed by the particles. After sufficient number of particles are formed that are able to absorb all of the radicals in the water phase, no new particles are formed in the water phase and the number of particles becomes constant. Also in homogeneous nucleation the particle number reaches a constant value, as in micellar nucleation. The subsequent growth stage is similar to the growth stage in the micellar nucleation.

*Particle Formation Rate*

The rate of particle formation by homogeneous nucleation can be derived by considering the water phase kinetics and rate of precipitation of the polymers at an assumed critical chain length (*jcr*). Assuming the aggregation number $(N_{agg})$ for the formation of stable particles from the precipitated precursor particles, the rate of particle formation by homogeneous nucleation is given by:

$$R_{homo} = \frac{dN}{dt} = \frac{N_a\left(\rho_i + k_{de}\bar{n}N / N_a\right)}{N_{agg}}\left(\frac{k_{pw}M_w}{k_{pw}M_w + k_{tw}R_w^{\bullet} + k_{ap}A_p + k_{am}A_m}\right)^{jcr+1} \quad \textbf{(4.26)}$$

In the above equation $R_w^{\bullet}$ refers to the concentration of live radicals in the water phase and is given by:

$$R_w^{\bullet} = \frac{\left(\rho_i + k_{de}\bar{n}N / N_a\right)}{k_{pw}M_w + k_{tw}R_w^{\bullet} + k_{ap}A_p + k_{am}A_m}\left(\frac{1-\beta^{jcr+1}}{1-\beta}\right) \quad \textbf{(4.27)}$$

Where:

$$\beta = \frac{k_{pw}M_w}{k_{pw}M_w + k_{tw}R_w^{\bullet} + k_{ap}A_p + k_{am}A_m} \quad \textbf{(4.28)}$$

Refer to Table 4.43 for the explanation of the symbols in the above equations.

## Particle Growth

Stage II, the growth stage, starts after the completion of the seed stage in the *in situ seed process*. In the in situ seed process, the micelles are used for the generation of the seeds. In the case of an *external seed process*, a well characterized seed is used as the starting material for emulsion production. If quality control tests indicate that the particle number and particle size distribution of the seed particles will not result in the desired end-product specifications, the batch is normally terminated. Therefore, in the growth stage it can be assumed that the desired number of particles, with the desired particle size distribution has already been formed.

It is generally agreed that the growth process is a well understood process and amenable to control. The growth reaction is responsible for developing molecular properties (molecular weights, composition, etc.) and morphology (core-shell, particle size distribution). Since the growth reaction lasts about 10-12 hours, there is great potential for optimizing the reaction time by increasing temperature or by keeping the particles saturated with monomer.

Once inside a particle, radicals induce the usual free-radical polymerization steps such as propagation, termination, chain transfer, etc. A growing radical can escape from a particle and return to the aqueous medium to participate in an aqueous phase termination reaction or enter into another particle. During Stage II, monomer continuously diffuses from the monomer droplets into the particle phase, providing a steady monomer supply for the growing polymer particle.

As the particles grow, the emulsifier molecules are continuously adsorbed onto or desorbed from the particles to maintain thermodynamic equilibrium. This dynamic exchange between various phases when added to the regular polymerization kinetics makes emulsion polymerization a more complex process than bulk or solution polymerization processes. Figure 4.12 illustrates these interactions.

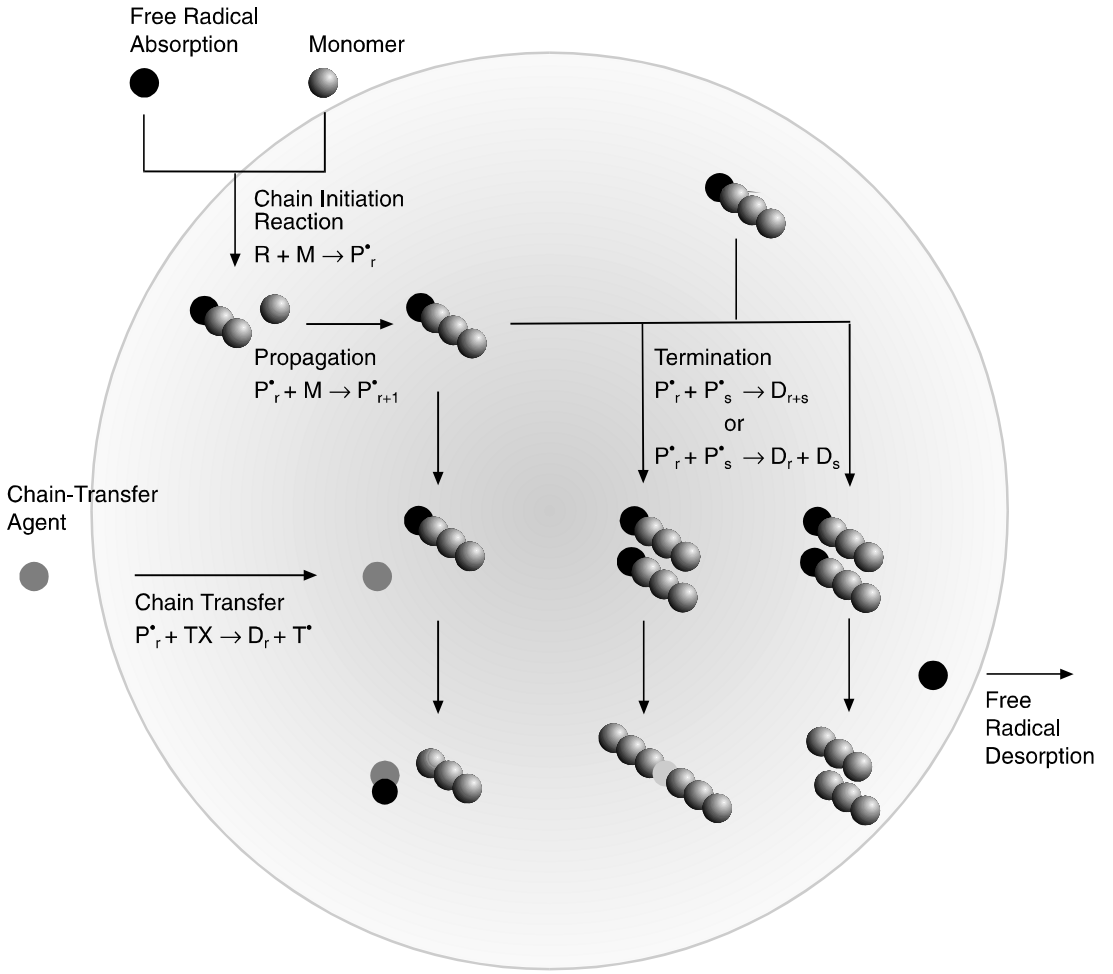


***Figure 4.12*** *Transport Processes and Reactions in a Latex Particle*

## Radical Balance

The radical balance in the aqueous phase is controlled by the kinetic events that are responsible for the radical generation and the radical consumption in that phase. Radicals are generated in the dispersant phase by two kinetic events:

- Initiator decomposition in the aqueous phase
- Desorption of radicals from the particle phase into the aqueous phase

Radicals are depleted from the aqueous phase by two kinetic events:

- Termination of a live radical with another live radical in the aqueous phase
- Diffusion of a radical from the aqueous phase into a particle or a micelle

*Aqueous Phase Rate*

The rate of production of radicals in the aqueous phase is considered equal to the rate of depletion of the radicals from the aqueous phase. This is an application of the stationary state hypothesis or quasi-steady-state approximation (QSSA):

$$k_{de}N_p\bar{n} + R_I N_a = k_a R_w^{\bullet} N_a + 2k_{tw}R_w^{\bullet 2}N_a \qquad \textbf{(4.29)}$$

Equation 4.29 can also be written as:

$$\alpha = \alpha' + m\bar{n} - Y\alpha^2 \qquad \textbf{(4.30)}$$

With:

$$\alpha = \frac{N_a^2}{N_p k_{tp}} = \frac{k_a R_w^{\bullet} N_a^2 \mathrm{v}}{N_p k_{tp}} \qquad \rho' = k_a R_w^{\bullet} \qquad \textbf{(4.31)}$$

$$\alpha' = \frac{R_I \mathrm{v}_s N_a^2}{N_p k_{tp}} \qquad \textbf{(4.32)}$$

$$m = \frac{k_{de}\mathrm{v}_s N_a}{k_{tp}} \qquad \textbf{(4.33)}$$

$$Y = \frac{2N_p k_{tp} k_{tw}}{k_a^2 \mathrm{v}_s N_a^2} \qquad \textbf{(4.34)}$$

Table 4.43 describes the emulsion polymerization model nomenclature.

### Table 4.43 Emulsion Polymerization Model Nomenclature

| Symbol | Description |
|---|---|
| $a_m$ | Area of a single micelle ( $m^3$ ) |
| $a_p$ | Area of a single particle ( $m^3$ ) |
| $A_m$ | Area of micelles ( $m^2$ / $m^3$ of aqueous phase) |
| $A_p$ | Area of particles ( $m^2$ / $m^3$ of aqueous phase) |
| $As$ | Area coverage by emulsifier ( $m^2$ / kmol ) |
| $d_p$ | Density of polymer ( kg / $m^3$ ) |
| $E$ | Emulsifier concentration ( kmol / $m^3$ ) |
| $F(\mathrm{v},t)$ | Volume density function for particle size distribution ( $m^{-3}$ ) |
| $f$ | Initiator efficiency |
| $[I]$ | Initiator concentration in the aqueous phase ( kmol / $m^3$ ) |
| $k_a$ | Absorption constant for particles ( $s^{-1}$ ) |
| $jcr$ | Critical chain length |
| $\varphi_p$ | Volume fraction of polymer in polymer particle |
| $k_d$ | Initiator dissociation constant ( $s^{-1}$ ) |
| $k_{de}$ | Rate constant for the desorption of radicals from the particles ( $m^3$ / s ) |
| $k_{am}$ | Rate constant for the absorption of radicals by micelles ( m / s ) |
| $k_{ap}$ | Rate constant for the absorption of radical by the particles ( m / s ) |
| $k_p$ | Rate constant for propagation in particle phase ( $m^3$ / kmol – s ) |
| $k_{pw}$ | Rate constant for propagation in the aqueous phase ( $m^3$ / kmol – s ) |
| $k_{act}^{ij}$ | Rate constant for activated initiation ( $m^3$ / kmol – s ) |
| $k_{ox}^{ij}$ | Rate constant for oxidation ( $m^3$ / kmol – s ) |
| $k_{re}^{ij}$ | Rate constant for reduction ( $m^3$ / kmol – s ) |
| $k_{tw}$ | Rate constant for the termination in the particle phase ( $m^3$ / kmol – s ) |
| $K_i^{pm}$ | Partition coefficient for the i-th component between polymer particles and monomer droplets |

*continued*

### *Table 4.43 Emulsion Polymerization Model Nomenclature (cont.)*

| Symbol | Description |
|---|---|
| $M_p$ | Concentration of monomer in the polymer phase ( Kmol / $m^3$ ) |
| $Mw_m$ | Molecular weight of monomer ( Kg / Kmol ) |
| $M_w$ | Monomer concentration in aqueous phase ( Kmol / $m^3$ ) |
| $\bar{n}$ | Average number of radicals per particle |
| $N_p$ | Number of particles per unit volume of aqueous phase ( no./$m^3$ ) |
| $N_a$ | Avogadro number |
| $N_{agg}$ | Aggregation number |
| $N_n$ | Number of particles containing n radicals per unit volume ( no./$m^3$ – s ) |
| $R_{homo}$ | Rate of particle generation by homogeneous nucleation ( no./$m^3$ – s ) |
| $R_w^{\bullet}$ | Radical concentration in the aqueous phase ( kmol / $m^3$ ) |
| $R_I$ | Rate of initiator dissociation ( kmol / $m^3$ – s ) |
| $t_{nuc}$ | Nucleation time(s) |
| $\mathrm{v}$ | Volume of a single unswollen particle ( $m^3$ ) |
| $\mathrm{v}_m$ | Volume of a single micelle ( $m^3$ ) |
| $\mathrm{v}_h$ | Volume of a single particle formed by homogeneous nucleation ( $m^3$ ) |
| $\dot{\mathrm{v}}$ | Volumetric growth rate of a single particle ( $m^3$ / s ) |
| $\mathrm{v}_s$ | Volume of a swollen particle ( $m^3$ ) |
| $\dot{\mathrm{v}}_s$ | Volumetric growth rate of a swollen particle ( $m^3$ / s ) |
| $\rho'$ | Rate of radical absorption by $N_p$ particles ( Kmol / s ) |
| $\rho_i$ | Total rate of radical generation ( Kmol / s - $m^3$ ) |
| $\nu_0$ | Zeroth moment of the particle size distribution ( no./$m^3$ of aqueous phase) |
| $\nu_1$ | First moment of the particle size distribution ( $m^3$ / $m^3$ of aqueous phase) |
| $\nu_2$ | Second moment of the particle size distribution ( $m^6$ / $m^3$ of aqueous phase) |
| $\nu_3$ | Third moment of the particle size distribution ( $m^9$ / $m^3$ of aqueous phase) |

Particles containing *n* radicals are produced by three kinetic events:

1. Absorption of a radical from the aqueous phase by a particle containing (*n*-1) radical. The total rate of this event is given as:

$$\frac{N_{n-1}\rho'}{N_p} \qquad \textbf{(4.35)}$$

2. Radical desorption from a particle containing (*n*+1) radicals. The total rate of this event is given as:

$$N_{n+1}k_{de}(n+1) \qquad \textbf{(4.36)}$$

3. Termination in a particle containing (n+2) radicals. The total rate of this reaction is given as:

$$\frac{N_{n+2}k_{tp}[(n+2)(n+1)]}{\nu} \qquad \textbf{(4.37)}$$

*Particle Phase*

Particles containing *n* free-radicals are depleted in the particle phase in three analogous ways. By equating the rate of formation to the rate of depletion of particles containing *n* free-radicals the recurrence formula is obtained:

$$N_{n-1}\left(\rho' N_a / N_p\right) + N_{n+1}k_{de}(n+1) + N_{n+2}k_{tp}\left(\frac{(n+2)(n+1)}{N_a \nu}\right) = N_n\left(\left(\rho' N_a / N_p\right) + k_{de}n + k_{tp}\frac{n(n-1)}{N_a \nu}\right)$$

**(4.38)**

This recurrence formula was first developed by Smith and Ewart, in a slightly modified form (Smith and Ewart, 1948). Equation 4.38 can be solved for the average number of radicals per particle, $\bar{n}$. The general solution as given by O'Toole is as follows (O'Toole, 1965):

$$\bar{n} = \frac{aI_m(a)}{4 \times I_{m-1}(a)} \qquad \textbf{(4.39)}$$

In Equation 4.39, $I_m(a)$ and $I_{m-1}(a)$ are modified Bessel functions of the first kind with parameters *m* and *a*. Equation 4.33 gives the definition of *m. a* is calculated as a function of $\alpha$, defined in Equation 4.31, according to:

$$a = \sqrt{8\alpha} \qquad \textbf{(4.40)}$$

The simultaneous solution for $\bar{n}$ (Equation 4.39) and the stationary steady state equation for the radical balance in the aqueous phase (Equation 4.29) completely define the kinetics of the emulsion polymerization.

# Kinetics of Emulsion Polymerization

A general emulsion polymerization kinetics scheme involves simultaneous free-radical polymerization taking place in the dispersant phase, particle phase and the monomer droplet phase. However, in general the monomer droplet phase is regarded as an inert phase supplying monomer to the particle phase during reaction. In conventional emulsion polymerization, initiator decomposition takes place in the dispersant phase and the initiator radicals enter the polymer particle phase.

The polymer particle phase is considered to be the site for all the polymerization reactions. There is a dynamic exchange of radicals between the particle phase and the dispersion phase. The average number of radicals per particle is dependent on the steady state that is reached as a result of this exchange. The free-radical kinetics scheme used in the model is that used in the free-radical polymerization model.

In addition to the kinetics previously described in the Free-Radical Polymerization section (Section 4.2), emulsion polymerization can also handle activated initiation, redox initiation, absorption and desorption.

*Activated Initiation*

The mechanism for activated initiation is given as:

$$I_k + A_j \xrightarrow{k_{act}^{kj}} n_{kj} R^{\bullet} + x*$$

Where:

$I_k$ = initiator molecule

$A_j$ = activator molecules which promote the dissociation of the initiator molecules

$R^{\bullet}$ = primary radical produced in the initiation reaction

$x*$ = waste products that do not participate in the polymerization reactions

In emulsion polymerization water soluble persulfate initiators are normally employed as initiators. In addition, water soluble sodium bisulfite is used as an activator in many emulsion polymerization reactions for accomplishing activated initiation of persulfates.

For the above given mechanism, $R_{act}^{kj}$ , the radical generation rate for activated initiation, is given by the following equation:

$$R_{act}^{kj} = \frac{dR^{\bullet}}{dt} = n_{kj} f_{kj} k_{act}^{kj} C_{I_k} C_{A_j}$$

Where:

$k_{act}^{kj}$ = rate constant for activated initiation

$C_{I_k}$ = concentration of initiator in the aqueous phase

$C_{A_j}$ = concentration of activator in the aqueous phase

$n_{kj}$ = number of radicals produced per initiator molecules

$f_{kj}$ = efficiency factor

*Redox Initiation*

The mechanism for redox initiation is given as:

$$I_k + Fe^{++} \xrightarrow{k_{ox}^{kj}} n_{kj} R^{\bullet} + Fe^{+++} + Y^* \quad \text{(slow)}$$

$$Fe^{+++} + A_j \xrightarrow{k_{re}^{kj}} Fe^{++} + x^* \quad \text{(fast)}$$

Similar to activated initiation, redox initiation is used in emulsion polymerization reactions to promote decomposition of initiators at a much lower temperature. For example, redox initiation is employed in cold rubber production. It is also used in emulsion polymerization reactions where high radical flux is needed.

In the above kinetic scheme, iron sulfate is used as the redox agent. As the ferrous and ferric ions get regenerated in the redox reaction, it is assumed that the total iron concentration remains constant in the reaction. As the rate of reduction is much faster than the rate of oxidation, a stationary state hypothesis is assumed for the ferrous and ferric ions.

Assuming stationary state hypothesis for the ferric and ferrous ion concentration in the redox initiation mechanism, it is easy to derive an equation for the rate of generation of the radicals by the redox initiation as follows:

$$R_{red}^{kj} = \frac{dR^{\bullet}}{dt} = n_{kj} f_{kj} \frac{k_{ox}^{kj} k_{re}^{kj} C_{I_k} C_{A_j} C_{Fe_t}}{k_{ox}^{kj} C_{I_k} + k_{re}^{kj} C_{A_j}}$$

Where:

$C_{Fe_t}$ = total concentration of the iron in the aqueous phase

$k_{ox}^{kj}$ = rate constant for oxidation step of the redox initiation

$k_{re}^{kj}$ = rate constant for reduction step of the redox initiation

$C_{I_k}$ = concentration of initiator in the aqueous phase

$C_{A_j}$ = concentration of activator in the aqueous phase

$n_{kj}$ = number of radicals produced per initiator molecules

$f_{kj}$ = efficiency factor

*Absorption and Desorption*

In addition, there is an exchange of radicals between the aqueous phase and the polymer phase. Radicals generated in the aqueous phase are absorbed by the micelles during micellar nucleation and by the particle during nucleation and subsequent growth. Radicals in the polymer phase can desorb from the particle and enter the aqueous phase. The kinetics of absorption and desorption are described as follows:

Absorption by particles:

$$R_j^{\bullet} + N_i \xrightarrow{k_{ap}} N_{i+1} \qquad R_{ap} = k_{ap} a_p C_{N_i} C_{R_j^{\bullet}}$$

Absorption by micelles:

$$R_j^{\bullet} + N_m \xrightarrow{k_{am}} N_1 \qquad R_{am} = k_{am} a_m C_{N_m} C_{R_j^{\bullet}}$$

Desorption:

$$N_i \xrightarrow{k_{de}} N_{i-1} + R^{\bullet} \qquad R_{de} = k_{de} i C_{N_i}$$

Where:

$a_m$ = area of a single micelle

$a_p$ = area of a single particle

$N_m$ = number of micelles with *i* radicals per cubic meter of aqueous phase

$N_i$ = number of particles with *i* radicals per cubic meter of aqueous phase

*Reaction Rate Constant*

The rate constant for each reaction in the built-in kinetics is calculated at the reaction temperature and pressure using the modified Arrhenius equation with user specified parameters for frequency factor, activation energy and activation volume:

$$k = k_o \exp\left(\frac{-Ea}{RT} - \frac{\Delta VP}{RT}\right)$$

Where:

$k_o$ = pre-exponential factor in l/sec for first order reactions, and $m^3 / kmol - s$ for second order reactions

$Ea$ = activation energy in mole-enthalpy units

$\Delta V$ = activation volume in volume/mole units

$P$ = reaction pressure

$R$ = universal gas constant

$T$ = reaction temperature

The second term in the exponential function contains the activation volume and is important for high pressure polymerization systems. The reactions are described in detail in Section 4.2.

Rate constants related to absorption by particles, absorption by micelles and desorption from particles are given by the Arrhenius expression as:

$$k = k_o \exp\left(\frac{-Ea}{RT}\right)$$

assuming zero activation volume.

# MODEL FEATURES AND ASSUMPTIONS

Following are the model features and assumptions used in the emulsion polymerization model available in Polymers Plus.

## Model Assumptions

The emulsion polymerization process is extremely complex and involves phenomena for which a complete theoretical understanding has not been reached. Important assumptions are made in the emulsion polymerization model:

- The reaction mixture is perfectly mixed
- Particles are formed by the micellar or the homogeneous mechanism
- No agglomeration or breakage of particles occurs
- No secondary nucleation occurs
- All particles have the same average number of radicals and hence the same volumetric growth rate
- The particle size distribution is unimodal, with moments of PSD sufficient to describe the PSD
- There are no mass transfer limitations on the polymerization reactions
- Molecular weight is controlled by chain transfer reactions

## Thermodynamics of Monomer Partitioning

Modeling of the kinetics involved in emulsion polymerization is complicated by the fact that the reaction mixture is multiphase. It is important to account for partitioning of the components among various phases. Up to four coexisting phases may be present in the reaction mixture. After the consumption of the monomer droplets, only three phases will remain in the system.

A short-cut methodology was used to handle the four phases. First, polymers are removed from the reaction mixture and the remaining mixture is flashed to yield 3 phases:

- Vapor phase - if present, contains water and monomers
- Dispersion phase - contains water
- Monomer phase - contains monomer and trace amount of water

The amount of monomer in the dispersion is determined by isofugacity relationships.

Next, the monomer phase is mixed with the polymer particles. Depending upon the homosaturation solubility of monomer components in the polymer, the resulting mixture may form a single phase (swollen polymer) or two phases (monomer saturated polymer and monomer droplets).

The mixture solubility is calculated as the weighted average of the individual component partition coefficients, $K_i^{pm}$. A $K_i^{pm}$ value of 0.5 on a mass basis or mole for a given component, means that at saturation the mass fraction of that component in the polymer phase is 0.5. All components which may be present in the monomer phase are allowed to partition.

The above mentioned strategy works well in systems where the monomer is sparingly soluble in water. However, there are situations in emulsion polymerization systems where a separate monomer phase is not formed at all. This happens when monomers are more soluble in water and are fed slowly (starved feed) such that a separate monomer phase is not formed.

In those situations, this strategy calculates zero monomers concentration in the polymer phase and hence is not correct. In order to predict monomer partitioning when a separate monomer is not formed, a partitioning algorithm based on the POLYNRTL model has been developed. A keyword PHOP has been added as a parameter to the reaction paragraph. When PHOP=3-LIQUID the algorithm assumes a maximum of three liquids in the reaction mixture and calculates monomer partitioning based on partition coefficient values. When PHOP=2-LIQUID the algorithm assumes two liquids in the reaction mixture and calculates monomer partitioning using the FLASH3 module available in Aspen Plus.

## Polymer Particle Size Distribution

Polymer particle size and size distribution, among other factors, determine the rheological properties of the latex. Although actual particle size distribution is important, it is often measured in terms of certain averages such as number average and weight average diameters. Further, rigorous tracking of the particle size distribution by discrete methods is computationally expensive.

In conventional emulsion polymerization where unimodal distributions are normally encountered, the moments of the particle size distribution give sufficient information about the nature of the particle size distribution. The particle size distribution can be described in terms of different independent variables such as diameter or volume of the particle. Since volumetric growth rate of the particle in emulsion polymerization remains almost constant in Stage I and Stage II of the process, the population balance equation is formulated in terms of the volume of the particles.

*General Population Balance Equation*

The general population balance equation for the emulsion polymerization is given as follows:

$$\frac{\partial F(\mathrm{v},t)}{\partial t}+\frac{\partial\left(\dot{\mathrm{v}}F(\mathrm{v},t)\right)}{\partial \mathrm{v}}=k_{am}A_m N_a\left[R^{\bullet}\right]_w\delta\left(\mathrm{v}-\mathrm{v}_m\right)+R_{homo}\delta\left(\mathrm{v}-\mathrm{v}_h\right) \quad \textbf{(4.41)}$$

In Equation 4.41 the right-hand side represents the nucleation of particles from miceller and homogeneous nucleation. The symbols were explained in Table 4.43. The volumetric growth rate is $\dot{\mathrm{v}}$ for a single unswollen particle (Equation 4.25):

$$\dot{\mathrm{v}}=\frac{k_p M_p \bar{n}}{N_a}\frac{MW_m}{d_p} \quad \textbf{(4.42)}$$

The general population balance equation can be converted to the equivalent moment equations. The *j*-th moment of the particle size distribution is given as:

$$\nu_j=\int_0^{\infty}\nu^j F(\nu,j)d\nu \quad \textbf{(4.43)}$$

Applying moment definition in Equation 4.43 to the general population balance equation in Equation 4.41, the first four moments of the particle size distribution are given as:

$$\frac{d\nu_0}{dt}=k_{am}A_m N_a[R^{\bullet}]_w+R_{homo} \quad \textbf{(4.44)}$$

$$\frac{d\nu_1}{dt}=\dot{\mathrm{v}}\nu_0+\mathrm{v}_m k_{am}A_m N_a[R^{\bullet}]_w+\mathrm{v}_h R_{homo} \quad \textbf{(4.45)}$$

$$\frac{d\nu_2}{dt}=2\dot{\mathrm{v}}\nu_1+\mathrm{v}_m^2 k_{am}A_m N_a[R^{\bullet}]_w+\mathrm{v}_h^2 R_{homo} \quad \textbf{(4.46)}$$

$$\frac{d\nu_3}{dt}=3\dot{\mathrm{v}}\nu_2+\mathrm{v}_m^3 k_{am}A_m N_a[R^{\bullet}]_w+\mathrm{v}_h^3 R_{homo} \quad \textbf{(4.47)}$$

Where:

$k_{am}$ = kinetic constant for the absorption of the oligomeric radicals into the micelles

$A_m$ = area of the micelles

$R_{homo}$ = rate of particle formation by homogeneous nucleation

# POLYMER PARTICLE PROPERTIES CALCULATED

The emulsion model is designed to generate the following results that are of interest for the emulsion polymerization process:

- Copolymer composition
- Number average molecular weight
- Particle size distribution averages for unswollen particles

The results are available as component attributes under the names listed in Table 4.44.

***Table 4.44 Component Attributes for Emulsion Polymers***

| Name | Symbol | Description | Class | Units |
|---|---|---|---|---|
| PSDZMOM | $\nu_0$ | Zeroth moment of the particle size distribution (volume) | 2 | no. / s |
| PSDFMOM | $\nu_1$ | First moment of the PSD (volume) | 0 | $m^3$ / s |
| PSDSMOM | $\nu_2$ | Second moment of the PSD (volume) | 2 | $m^6$ / s |
| PSDTMOM | $\nu_3$ | Third moment of the PSD (volume) | 2 | $m^9$ / s |
| VOLN | $V_n$ | Number average volume of the particles | 0 | $m^3$ |
| VOLV | $V_v$ | Volume average volume of the particles | 0 | $m^3$ |
| VOLZ | $V_z$ | Z-average volume of the particles | 0 | $m^3$ |
| DIAV | $D_v$ | Volume average diameter | 0 | m |
| PDV | $PD_v$ | Polydispersity for PSD (Volume) | 0 | --- |
| SFRAC | --- | Copolymer composition | 0 | --- |
| MWN | --- | Number average molecular weight | 0 | kg / kmol |

## User Profiles

In addition to the polymer properties reported through the component attributes, other model calculations are reported through User Profile variables. The following user profile variables may be requested from the model:

- Glass transition temperature of the polymer (°C)
- Average number of radicals per particle
- % Soap coverage of the polymer particles
- Volume of the monomer droplet phase ( $m^3$ )
- Concentration of monomers in the monomer droplets ( $kmol / m^3$ )†
- Volume of the aqueous phase ( $m^3$ )
- Monomer concentration in the aqueous phase ( $kmol / m^3$ )†
- Volume of the polymer particle phase ( $m^3$ )
- Monomer concentration in the polymer particles ( $kmol / m^3$ )†
- Monomer conversion

† One profile is reported for each monomer.

User profiles are only accessible if the reaction model is called from a batch reactor (RBATCH) or a plug flow reactor (RPLUG). The user profiles are returned in the order shown. A label must be provided to differentiate the profile variables. For the monomer concentrations in the aqueous, monomer, and polymer phases one profile is returned for each monomer.

# SPECIFYING EMULSION POLYMERIZATION KINETICS

## Accessing the Emulsion Model

To access the Emulsion polymerization kinetic model:

1. From the Data Browser, find the **Reactions** folder.
2. From the **Reactions** folder, select **Reactions** again to get to the Reactions object manager.

   If the kinetic model already exists, double-click on the desired Reaction ID in the object manager or select **Edit** to get to the input forms.
3. To add a new model, from the **Reactions** object manager, select **New**. If necessary, change the default ID for the reaction.
4. Select Emulsion as the reaction type and click on **OK**.

## Specifying the Emulsion Model

The Emulsion model input forms are divided into two folders: Specifications and Phases.

Use the **Specifications** folder to define reacting species and enter reaction rate constant parameters. Use the following options:

| Use this sheet | To |
|---|---|
| Species | Define reacting species |
| Reactions | Specify reactions and rate constant parameters |
| Rate Constants | Summarize rate constant parameters |
| Options | Select additional options |
| Gel Effect | Gel-effect correlation parameters |

Use the **Phases** forms to enter information related to phase partitioning and particle growth. Use the following options:

| Use this sheet | To |
|---|---|
| Phase Equilibria | Specify component phase split |
| Particles | Specify emulsifiers and define particle radical exchange information |

## Specifying Reacting Species

You must specify the reacting species in the **Specifications Species** sheet:

1. In the **Polymer** field, specify the polymer produced. Also specify **Dispersant** and **Redox** agent.
2. In the Monomers field list the reacting monomers. For each monomer, in the **goes to** → field specify the polymer segment which the monomer converts to.
3. Continue listing other types of reacting species, e.g. solvents, transfer agents, etc.
4. Select the **Generate Reactions** option if you would like the reactions to be generated automatically.

   After going through the reaction generation once, it is recommended that you turn off this feature. Otherwise, the reaction generation will be performed repeatedly.

## Listing Reactions

The Emulsion model generates reactions based on the list of reacting species. You can view the system-generated reactions, then assign rate constant parameters to these reactions.

You can view a list of the system-generated reactions on the Specifications Reactions sheet. In the Reaction summary listing, for each reaction the first column indicates the reaction type. The second column lists the reactants, and the last column lists the products. The Data Browser window can be resized to better view the reaction listing. Use the following options:

| Click on | To |
|---|---|
| New | Add new reactions to the scheme |
| Edit | Edit the current reaction indicated by the row selector |
| Rate Constants | Specify reaction rate constant parameters for the reactions |

Click to select a reaction. Click a reaction then Control-Click to include additional reactions for multiple selection. Double-click to edit a reaction.

In addition, you may use the following buttons:

| Click on | To |
|---|---|
| Hide/Reveal  | Exclude/Include a reaction from the calculations |
| Delete  | Permanently remove a reaction from the model |

## Adding Reactions

To add a new reaction to the scheme, click on **New** to open the Add Reaction subform. When you open the Add Reaction subform:

1. In **Reaction type**, select a type for the new reaction. The **Reaction scheme** for that type is displayed.
2. In other reactant (e.g. **Initiator**, **Catalyst**) fields enter the reactants of the categories allowed for that reaction type.
3. Click on **Cancel** to discard the new reaction

   – or –

   Click on **New** to add a new reaction

   – or –

   Click on  to check the **Completion status**

   – or –

   Click on **Done** to return to the reaction summary.

## Editing Reactions

To edit a reaction, click on **Edit** to open the Edit Reaction subform. When you open the Edit Reaction subform:

1. Modify the **Reaction type** as needed.

   The **Reaction scheme** for that type is displayed.
2. Modify reactants as needed.
3. Click on  to check the **Completion status**

   – or –

   Click on **Done** to return to the reaction summary.

## Assigning Rate Constants to Reactions

To assign rate constants to user reactions, click on **Rate Constants** to open the Rate Constant Parameters subform:

1. In the **Ko** field, enter the pre-exponential factor.
2. In the **Ea** field, enter the activation energy.
3. In the **ΔV** field, enter activation volume.
4. In the **Tref** field, enter reference temperature.
5. In the **Efficiency** field, enter initiator efficiency for initiation reactions.
6. In the **No. radicals** field, enter the number of primary radicals formed in initiation reactions.
7. Click on the stoichiometry list and select a new reaction to enter rate constants for another reaction. You can use the **Prev** and **Next** buttons to select the previous or next reaction in the list.
8. Click on the Summary tab to see a listing of all the rate constant parameters.
9. Click on  to check the **Completion status**

   – or –

   Click on **Close** to return to the reaction summary.

## Selecting Calculation Options

You can select additional simulation options for the model such as special initiation options, and gel-effect on the Options tab sheet.

For special initiation, specify the monomers affected, then enter the special initiation coefficients. For Gel effect, you need to specify parameters on the **Gel Effect** sheet.

## Adding Gel-Effect

Use the Gel-Effect sheet to add gel effect to reactions:

1. Enter a unique integer identifier in **No**.
2. In the **Reaction** field, specify the reaction to which you would like to apply gel effect.
3. In the **Corr. No.** field, specify a gel effect correlation number.
4. In **Parameters**, list the parameters for the gel effect correlation.

## Specifying Phase Partitioning

Use the Phases Phase Equilibria sheet to specify phase partitioning for the components in the emulsion system:

1. If you select a **Rigorous** approach, specify a **Method**.
2. If you select the **Partition Coefficients** approach, in the **Basis** field select the phase partitioning basis, e.g. mole or mass.
3. For each component, specify the split fraction in the **Component** and **Coefficient** fields.

## Specifying Particle Growth Parameters

Use the Phases Particles sheet to specify data for particle generation and particle related events:

1. Define **Emulsifier**, and specify critical micelle concentration, **CMC**, and surfactant **Area**.
2. For homogeneous nucleation, specify **Aggregat no.** and **Critical length**.

You must specify radical absorption and desorption rate constant parameters for micelles and particles.

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# 4.4 ZIEGLER-NATTA POLYMERIZATION MODEL

This section covers the Ziegler-Natta polymerization kinetic model available in Polymers Plus. The term Ziegler-Natta polymerization is used here to describe a variety of stereospecific multi-site and single site catalyzed addition polymerization systems including the traditional Ziegler-Natta catalyzed systems, chromium based catalyzed systems (Phillips type) and the more recent metallocene based catalyzed systems.

Topics covered include:

- Summary of Applications
- Ziegler-Natta Processes
- Reaction Kinetic Scheme
- Model Features and Assumptions
- Polymer Properties Calculated
- Specifying Ziegler-Natta Polymerization Kinetics

Several example applications of the Ziegler-Natta polymerization model are given in the *Polymers Plus Examples & Applications Case Book*. The *Examples & Applications Case Book* provides process details and the kinetics of polymerization for specific monomer-polymer systems.

# SUMMARY OF APPLICATIONS

The Ziegler-Natta polymerization model is applicable to processes utilizing coordination catalysts for the production of stereospecific polymers. Some examples of applicable polymers are:

- Linear low density polyethylene - Ethylene is copolymerized with an alpha-olefin, such as 1-butene, 1-hexene, or 1-octene. Commercial processes include low pressure, slurry-phase processes, solution-phase processes, low pressure, gas phase processes.
- High density polyethylene - Ethylene homopolymers or copolymers with high alpha olefins with density 0.940 $g / cm^3$ and higher. Commercial processes include solution, slurry or suspension, and gas phase polymerization.
- Ethylene-propylene elastomers - Polymerization proceeds by solution or slurry processes. Both are operated continuously in liquid-phase back-mixed reactors.
- Polypropylene - Commercial processes include liquid pool, diluent slurry, and gas phase polymerization.

# ZIEGLER-NATTA PROCESSES

Ziegler-Natta polymerization accounts for a significant fraction of the polyethylene polymers and all the polypropylene homopolymers and copolymers produced commercially. The commercial production of these polyolefins is done exclusively by continuous processes using several different processes and reactor types operating over a wide range of conditions.

High density polyethylene (HDPE) and linear low density polyethylene (LLDPE) are produced via catalyzed polymerization processes. The operating conditions for the catalyzed processes are relatively less severe compared to the high pressure processes for LDPE production. The pressure generally ranges from 10-80 atm while the temperatures range from 80-110°C. The pressure and temperature may be as high as 200 atm and 250°C in some of the solution polymerization processes.

## Catalyst Types

There is a variety of catalysts used for ethylene polymerization including *supported* and *unsupported* heterogeneous catalyst systems and homogeneous catalyst systems. The Ziegler-Natta transition metal (Ti) based catalysts are the most widely used.

However, there are numerous variations of these catalysts. Some vanadium based catalysts are also used. Chromic oxide on silica catalysts are used in the Phillips loop reactor process, while the Union Carbide Unipol process may use either Ziegler-Natta (Ti) or chromium compounds on silica catalysts.

More recently, several manufacturers have been developing commercial processes using metallocene based catalysts, mainly zirconium and titanium. These catalysts are believed to be single site catalysts that are capable of producing high yields, combined with narrow molecular weight and copolymer composition distributions.

All commercial isotactic polypropylene homopolymer (PP) is manufactured using heterogeneous Ziegler-Natta catalyst systems. The catalyst consists of a solid transition metal halide, usually $TiCl_3$, with an organoaluminum compound cocatalysts, such as diethylaluminum chloride (DEAC), or a $MgCl_2$ supported $TiCl_4.AlEt_3$ catalyst.

## Ethylene Process Types

There are three types of catalyzed ethylene polymerization processes in commercial use today:

- Liquid slurry
- Solution
- Gas-phase

A partial list of these processes is given in Table 4.45 along with a summary of their characteristics.

In the slurry process, a hydrocarbon diluent is used, typically a $C_4 - C_7$ paraffin, isoparaffin or cycloparaffin. Under the conditions used the polyethylene is essentially insoluble in the diluent. As a result a slurry is formed.

In the solution process, the conditions used are such that the polyethylene is completely dissolved in the solvent.

In gas-phase processes, gaseous ethylene and comonomers are contacted with a polymer-catalyst powder. Polymerization occurs in the monomer-swollen polymer particles which contain embedded catalyst fragments with active sites.

Ethylene polymerization processes have been reviewed extensively. More detailed descriptions of these processes are available in the open literature (Short, 1983; Choi and Ray, 1985a; Nowlin, 1985; Albright, 1985).

***Table 4.45 Characteristics of Processes for HDPE and LLDPE Manufacture***

| Process | Reactor | Diluent / Solvent | Catalyst | Temp. (°C) | Press. (atm) | Residence Time (hr) | Company |
|---|---|---|---|---|---|---|---|
| Liquid slurry | Loop | i-butane<br>n-hexane | Supported Ti or Cr | 80-100 | 30-35 | 1.5-2.5 | Phillips Solvay |
| | CSTR | n-hexane | Supported Ti | 80-90 | 8-35 | 2.0-2.7 | Dow<br>Hoechst<br>Nissan<br>Mitsubishi<br>Montedison |
| Solution | CSTR | n-hexane<br>cyclohexane | Ti/V | 130-250 | 30-200 | 0.08-0.17 | Dow<br>Dupont<br>Stamicarbon |
| Gas | Stirred bed | --- | Supported Ti or Cr | 70-110 | 20-35 | 3-5 | AMOCO<br>BASF |
| | Fluidized bed | --- | Supported Ti or Cr | 85-100 | 20-30 | 3-5 | BP<br>Union Carbide |

## Propylene Process Types

There are three types of catalyzed polypropylene homopolymerization processes in commercial use today:

- Liquid slurry
- Liquid pool (bulk)
- Gas-phase

A partial listing of these processes along with a summary of their characteristics is given in Table 4.46.

In the slurry process, a hydrocarbon diluent, typically butane, hexane or heptane, is used at operating temperatures of 70-90°C. Under these conditions the isotactic polypropylene is essentially insoluble in the diluent. As a result a slurry is formed.

In the liquid pool process, liquid propylene is used in place of the diluent. In this process also, the polypropylene is insoluble in the liquid propylene and a slurry is formed. The higher monomer concentrations in this process allow for smaller reactors and lower operating temperatures compared to the slurry process.

In the gas-phase processes, gaseous propylene is contacted with a polymer-catalyst powder. Polymerization occurs in the monomer-swollen particles which contain embedded catalyst fragments with active sites.

Propylene polymerization processes have been reviewed extensively in the literature. More detailed descriptions of these processes are available in the open literature (Brockmeier, 1983; Choi and Ray, 1985b; Albright, 1985).

Besides polypropylene homopolymer (PP), high impact polypropylene (HIPP) and some ethylene-propylene (EP) copolymers are produced by including an additional reaction stage to the polypropylene homopolymerization process. A summary of their characteristics is given in Table 4.47.

In the EP process, last reaction stage is designed to introduce the desired amount of EP copolymer into the PP product. For example, the Himont spheripol process uses liquid pool loop reactors followed by a gas-phase fluidized bed reactor for the copolymerization stage. The residence time distribution of the polymer particles leaving each stage should be as narrow as practical to ensure that the weight ratio of EP to PP for particles leaving the second stage is as uniform as possible. The Amoco/Chisso process has largely met this requirement.

### *Table 4.46 Characteristics of Processes for Propylene Homopolymerization*

| Process | Reactor | Diluent / Solvent | Catalyst | Tacticity (%) | Temp. (°C) | Press. (atm) | Residence Time (hr) | Company |
|---|---|---|---|---|---|---|---|---|
| Bulk (Liquid Pool) | Loop | Liquid monomer | Supported Ti | Up to 99 | 60-80 | 30-40 | 1-2 | Himont<br>Mitsui |
| | CSTR | Liquid monomer | Unsupported or supported Ti | Up to 98 | 60-75 | 30-40 | 2 | Dart<br>El Paso<br>Montedison<br>Sumitomo |
| Diluent Slurry | CSTR | n-hexane, n-heptane | Unsupported or supported Ti | Up to 98 | 60-80 | 15-20 | 3-4 | Montedison |
| Gas | Fluidized bed | N2 | Supported Ti | Up to 98 | 60-80 | 20 | 3-5 | Sumitomo<br>Union Carbide |
| | Vertical stirred bed | --- | Unsupported or supported Ti | Up to 98 | 70-90 | 20 | 4 | BASF<br>ICI<br>USI |
| | Horizontal compartmented stirred bed | --- | Unsupported or supported Ti | Up to 98 | 70-90 | 20 | 4 | AMOCO |

## *Table 4.47 Catalyst Processes for Propylene Copolymerization*

| Process | Reactor | Diluent / Solvent | Catalyst | Temp. (°C) | Press. (atm) Stage 1 | Press. (atm) Stage 2 | Residence Time (hr) | Comonomers | Company |
|---|---|---|---|---|---|---|---|---|---|
| Bulk (Liquid Pool) + Second Stage | Loop - fluid bed | --- | Supported Ti | 60-80 | 30-40 | 20 | 1-2 | Ethylene & others | Himont<br>Mitsui |
| | CSTR - CSTR | --- | Supported Ti | 60-75 | 30-40 | 30-40 | 2 | Ethylene | Sumitomo |
| | CSTR - stirred horizontal bed | --- | Unsupported or supported Ti | 40-75 | 30-40 | 20 | 2-5 | Ethylene | Dart<br>El Paso |
| Diluent Slurry | CSTR | Liquid monomers & diluents | Ti/V | 0-20 | 5-20 | --- | 1 | Ethylene, Butene, dienes | Montedison<br>Dutral |
| Multistage Gas | Fluid bed - fluid bed | --- | Supported Ti | 60-80 | 20 | 20 | 3-5 | Ethylene & others | Sumitomo<br>Union Carbide |
| | Vertical stirred bed - stirred bed | --- | Unsupported of supported Ti | 70-90 | 20 | 20 | 4 | Ethylene & others | BASF<br>ICI<br>USI |
| | Horizontal stirred bed - horizontal stirred bed | --- | Supported Ti | 70-90 | 20 | 20 | 4 | Ethylene & others | AMOCO<br>Chisso |

# REACTION KINETIC SCHEME

The built-in catalyst/polymerization kinetic scheme represents the typical scheme described in the open literature (Xie et al., 1994). Although a number of reaction mechanisms have been proposed to describe stereospecific Ziegler-Natta polymerization, there is still no definitive reaction mechanism to completely describe the kinetic behavior of these complex catalyst/polymerization systems.

Most of the proposed mechanisms include a detailed set of reactions. However, not all of these reactions apply to every catalyst system nor can they be verified. The kinetic scheme for chromium and metallocene catalyzed systems can be considered to be a subset of a comprehensive Ziegler-Natta kinetic scheme.

*Key Elementary Reactions*

There are a few key elementary reactions that apply to almost all catalyzed addition polymerization systems. These include the three basic reaction steps:

- Chain initiation
- Propagation
- Chain transfer (spontaneous and to small molecules such as monomer, solvent and chain transfer agents)

For chromium and metallocene catalyst systems, additional reactions for long chain branching via terminal double bond polymerization must also be included.

In addition to the polymerization reactions, there are reactions affecting the catalyst active sites on which the polymerization reactions take place. These include catalyst site activation, inhibition and deactivation. The catalyst reactions and the polymerization reactions occur simultaneously during the polymerization.

A comprehensive kinetic scheme for the catalyzed multi-site homo- and copolymerization of any number of monomers has been built into Polymers Plus.

*Catalyst States*

The catalyst states and the types of reactions affecting them are shown in Figure 4.13. In setting up a simulation, the user specifies the catalyst flow rate for the feed streams, and a catalyst parameter, the moles of sites per unit mass of catalyst. This parameter together with the catalysts flow rate is used to compute the total moles of sites.

The total moles of sites are made up of potential sites, active sites of different reactivities, and dead sites. Site activation reactions convert potential sites to active sites, while site deactivation reactions convert active sites to dead sites. There are several different site activation/deactivation reactions built into the kinetic scheme and these are discussed later in this section.

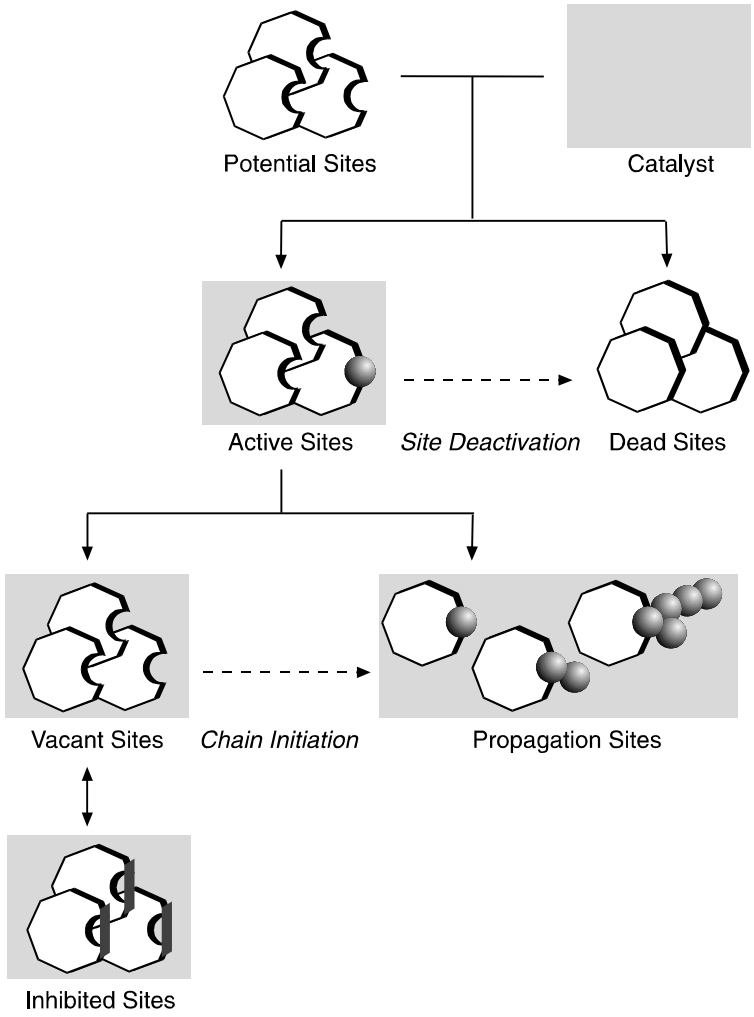


***Figure 4.13*** *Schematic Description of Multi-Site Catalyst States*

*Site Types*

In this figure, potential sites and dead sites are considered to be independent of site type. The user specifies the number of site types to be included for a particular simulation.

- A vacant site is an active site that does not have a polymer or other molecule attached to it.
- A propagation site has a growing polymer molecule attached to it.

When a vacant site is involved in a chain initiation reaction it is converted to a propagation site. Inhibited sites have small molecules such as hydrogen or poisons attached.

As a result, inhibited sites are temporarily blocked from becoming propagation sites. The site inhibition reaction is considered reversible. Therefore, the small molecule may dissociate from an inhibited site which then becomes a vacant site once again.

The built-in catalyst and polymerization kinetic scheme is shown in Figure 4.14. The scheme includes most of the reactions commonly used for modeling Ziegler-Natta polymerization. Reactions such as depropagation, internal double-bond polymerization with diene comonomers, and site transformation reactions (Debling et al., 1994; Xie et al., 1994) have not been included in the current model. These reactions may be added to the built-in scheme in the future.

*Kinetic Scheme Nomenclature*

The nomenclature used in the kinetic scheme is given in Table 4.48. In the following discussion:

- A polymer chain is considered to be made up of monomer units or segments derived from the propagating monomers
- *Live chain* $(P_{n,i}^{k})$ refers to growing polymer chains containing *n* segments or monomer units, with an active segment of type *i* attached to a catalyst active site of type *k*
- *Dead chain* $(D_{n}^{k})$ refers to a terminated polymer chain
- The superscript *k* refers to the active site type from which the dead polymer chain was formed
- The subscript *n* refers to the chain length in terms of the number of segments or monomer units incorporated in the polymer chain

Live chains are reactive and can participate in the polymerization reactions while dead chains are usually considered inert, except in cases where long chain branching reactions are important.

*Polymerization Mechanism*

The catalyst active site is attached to one end of a live polymer chain via a metal-carbon bond. It is generally accepted that polymerization proceeds via a two-step mechanism. In the first step, monomer is complexed to the transition metal site. The second step is the coordinated insertion of the monomer into the metal-carbon bond. As a result, the polymer chain and the previously added segments grow away from the active site with every addition of a monomer molecule.

It is believed that the chain microstructure will not have a strong influence on the mode of monomer addition. For this reason, the built-in kinetic model assumes that the reactivity of a live polymer chain depends only on the active segment and the active site type, and is independent of the polymer chain length and other structural properties. Meaning in the propagation reaction, the rate of propagation $R_{p,ij}^{k}$ is independent of the polymer chain length. It depends only on the concentration of monomer *j*, and the concentration of live polymer chains with active segments of type *i* attached to an active site of type *k*. Models using this assumption are referred to as *terminal models* in the polymerization literature.

*Copolymerization Mechanism*

For copolymerization, the built-in kinetic scheme allows the user to specify the number of monomer types used. Similarly the user has the flexibility to specify the number of each type of reactive species present in the polymerization: catalysts, cocatalysts, chain transfer agents, solvents, etc. The user is able to tailor the built-in kinetics to model a specific catalyzed polymerization system by selecting a subset of the reactions shown in Figure 4.14. However, it is important that the subset include a chain initiation, propagation, and at least one chain transfer or active site deactivation reaction to produce dead polymer.

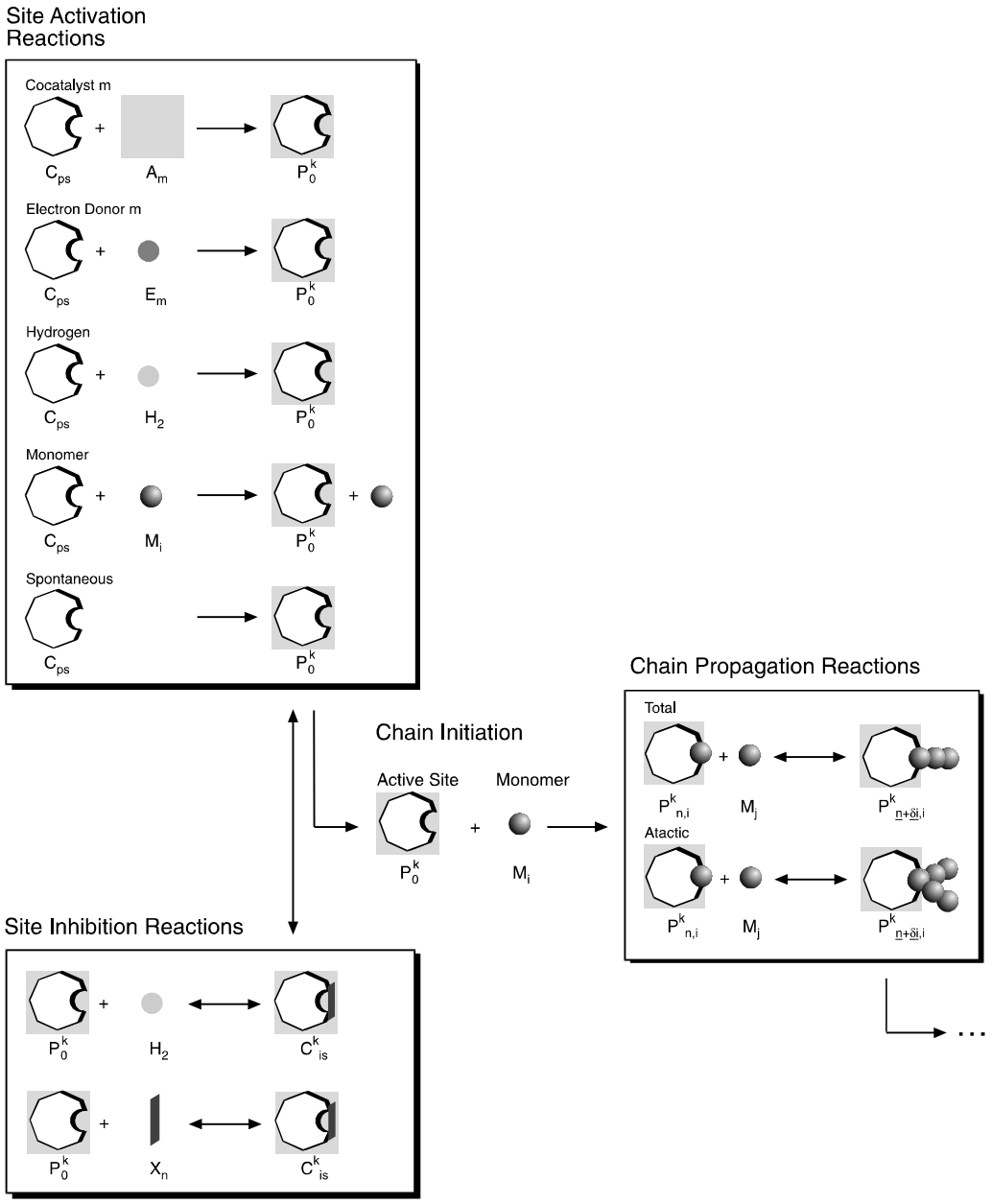


***Figure 4.14*** *Built-In Ziegler-Natta Catalysts and Polymerization Kinetic Scheme*

*continued*

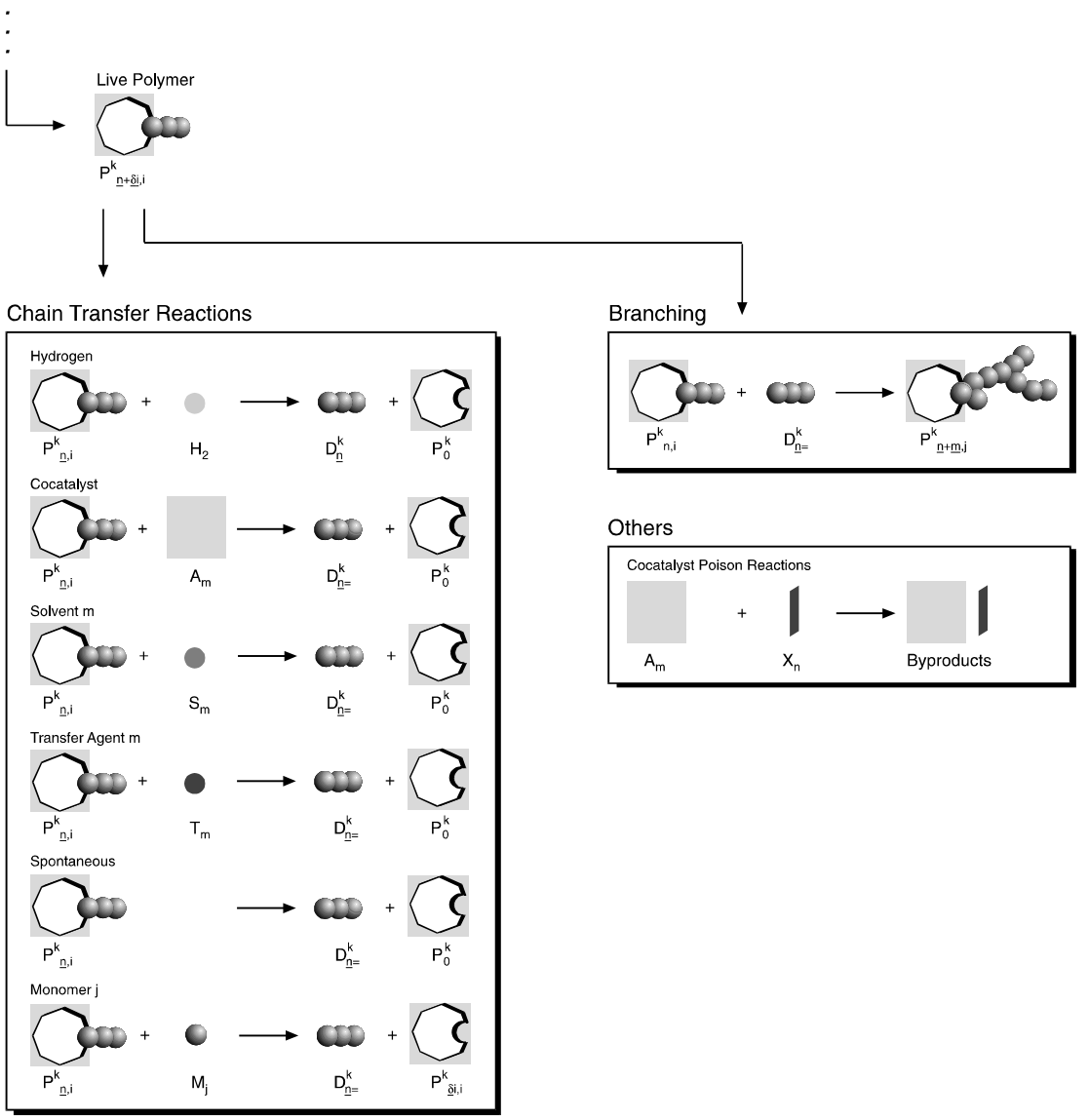


***Figure 4.14*** *Built-In Ziegler-Natta Catalysts and Polymerization Kinetic Scheme (cont.)*

*continued*

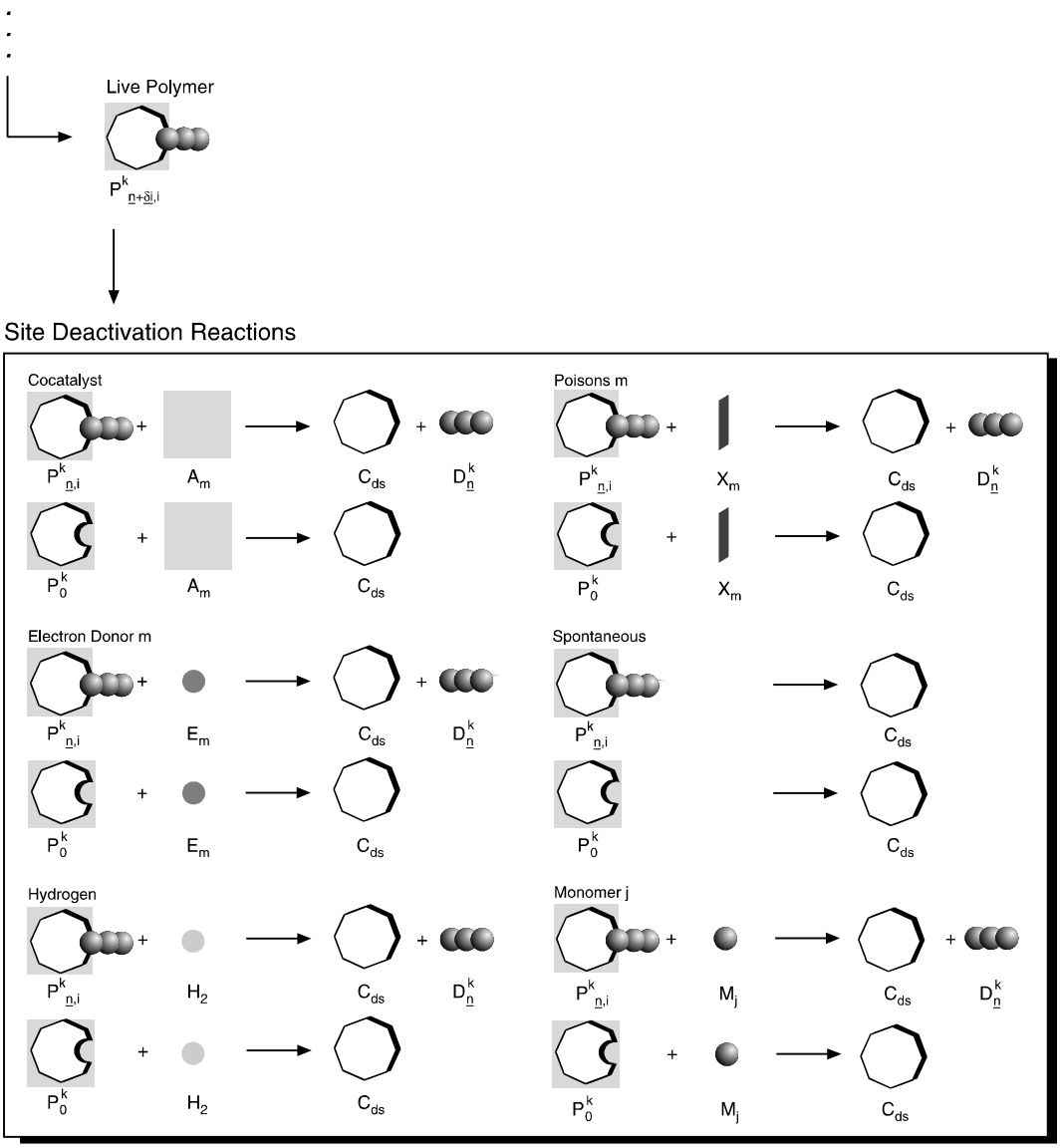


***Figure 4.14*** *Built-In Ziegler-Natta Catalysts and Polymerization Kinetic Scheme (cont.)*

### Table 4.48 Ziegler-Natta Polymerization Kinetics Nomenclature

| Symbol | Description |
|---|---|
| $A_m$ | Cocatalysts m |
| $E_m$ | Electron donor m |
| $C_{ds}$ | Dead catalyst sites |
| $C_{ps}$ | Potential catalyst sites |
| $C_{is}^k$ | Inhibited catalyst sites of type k |
| $D_n^k$ | Dead polymer chain of length n $(= n1,\ n2,\ ...,\ n_m)$ for copolymerization produced from a catalyst site of type k |
| $H_2$ | Hydrogen |
| $M_j$ | Monomer j |
| $N_m$ | Number of monomers |
| $N_{sites}$ | Number of active site types |
| $O^k$ | Reaction order for the non-polymer component at site type k |
| $P_0^k$ | Vacant catalyst sites of type k |
| $P_{n,i}^k$ | Live polymer chain of length n having an active segment of type i attached to a active site of type k |
| $S_m$ | Solvent m (for solution or slurry polymerization) |
| $T_m$ | Chain transfer agent m |
| $X_n$ | Inhibitor n |
| $\mu_{0,i}^k$ | Zeroth moment of live polymer with respect to active segment of type i and active site of type k |

*Rate Expressions*

The rate expressions for each of the reactions in the kinetic scheme are also listed in Figure 4.14. The rate is generally written as a product of the rate constant and the concentrations of the reacting species. In many of the reactions, one of the reacting species is a polymer chain while the other is a small molecule such as monomer, chain transfer agent, cocatalyst, etc. A reaction order with respect to the small reacting molecule is included for some of the reactions. This reaction order has a default value of one.

The rate constants for each reaction at sites of type *k* are calculated at the reaction temperature using the Arrhenius equation shown below. The user specified rate constant parameters are pre-exponential factor $(k_o^k)$ and the activation energy $(Ea^k)$ at sites of type *k*.

*Rate Constant*

$$k^k = k_o^k \exp\left(-\frac{Ea^k}{RT}\right)$$

Where:

$k_o$ = pre-exponential factor in 1/sec for first order reactions and $m^3 / kmol - \sec$ for second order reactions

$Ea$ = activation energy in mole enthalpy units

$R$ = universal gas constant

$T$ = temperature in Kelvin

## Catalyst Site Activation

The catalyst site activation step involves the generation of reactive vacant active sites from potential sites. Depending on the catalysts system, the activation may be done before the catalyst is fed to the reactor or within the reactor.

There are several different site activation reactions included in the built-in kinetic scheme. They include site activation by cocatalyst, by electron donors, by hydrogen, by monomer, and spontaneous site activation. Different catalyst systems tend to be activated by a different subset of the reactions in this scheme. For example, $TiCl_3$ catalyst systems are usually activated with an organoaluminum cocatalyst such as diethylaluminum chloride (DEAC), in the reactor. Chromic oxide catalysts are calcined by heating with air for several hours at temperatures of 400°C to 975°C and cooled in dry air. Some of these catalysts may be activated with a reducing agent before introduction into the reactor, while others are activated within the reactor.

*Site Activation Reactions*

Some of the site activation reactions (activation by monomer, electron donor, hydrogen) have been proposed to explain the observed rate enhancement behavior in different catalyst systems. For example, the activation of additional sites by comonomer has been proposed to explain the rate enhancement observed with the addition of a comonomer to ethylene and propylene homopolymerization reactors.

## Chain Initiation

Chain initiation involves the reaction of a monomer molecule at a vacant active site to form a live polymer molecule of unit length at that site. This reaction converts a vacant active site to a propagation site. The chain initiation reaction is shown below:

$$P_o^k + M_i \rightarrow P_1^i \qquad R_{ci}^k = k_{ci}^k P_o^k \left(C_{Mi}\right)^{O_{Mi}^k}$$

The rate of chain initiation at site type $k$ $(R_{ci}^k)$ is dependent on the concentration of vacant sites of type $k$ and the concentration of monomer $i$. The user can also specify the reaction order with respect to the monomer concentration. The live polymer chains grow by successive addition of monomer molecules to form long polymer molecules.

## Propagation

The live polymer at each active site type grow or propagate through the addition of monomer molecules to form long polymer chains. The propagation reaction is represented by:

$$P_{n,i}^k + M_j \rightarrow P_{n+1,j}^k \qquad R_{p,ij}^k = k_{p,ij}^k C_{Mj} P_{n,i}^k \text{ (main propagation)}$$

Where monomer $j$ is being added to a polymer chain of length $n$, with an active segment of type $i$ at an active site of type $k$. The resulting polymer chain will be of length $n$+1 and the active segment will be of type $j$. The active segment type usually represents the last monomer type incorporated into the polymer chain.

For copolymerization, there will be $N_m * N_m * N_{site}$ propagation reactions that may have different reactivities. For example, with two monomers and three site types, the monomer being added could be monomer 1 or monomer 2 while the active segment type could be segments from monomer 1 or monomer 2 at each site type.

As a result, there will be twelve rate constants $(k_{p,ij}^k)$, where the subscript $i$ refers to the active segment type while the second subscript $j$ refers to the propagating monomer type. The superscript $k$ refers to active site type. For the terminal model the rate of propagation is dependent only on the concentration of live polymer with active segment $i$ at active site $k$ and the concentration of the propagating monomer $j$.

In Polymers Plus Version 3.0 and higher, another propagation reaction has been added to account for formation of atactic polymer. This reaction has the same form as the main propagation reaction:

$$P_{n,i}^k + M_j \rightarrow P_{\underline{n}+\underline{\delta}i,i}^k \qquad R_{paij}^k = k_{paij}^k \mu_{0,j}^k \left(C_{Mi}\right)^{O_{paMi}^k} \text{ (atactic propagation)}$$

but uses a different rate constant $(k_{paij}^{k})$. When the atactic propagation reaction is included in the simulation, the main propagation reaction should be considered to account for the formation of all polymer whether it is isotactic or atactic. Hence the main propagation reaction is also termed the total propagation. The atactic propagation reaction only accounts for the formation of atactic polymer. The atactic content of the polymer is then calculated from the ratio of atactic to total polymer.

## Chain Transfer to Small Molecules

Chain transfer to small molecules such as monomer, solvent or chain transfer agent usually involves the extraction of hydrogen from the small molecule by the active site and leads to the termination of the live chain. At the same time, a new vacant site is formed which can undergo chain initiation to start polymerization. The effect of chain transfer on the polymerization kinetics depends on the reactivity of the transfer sites.

When the transfer site is very reactive, as is the case when the chain initiation rate constant is greater than the propagation rate constant, chain transfer will not lower the polymerization rate or conversion, but will reduce the molecular weight of the polymer. However, if the transfer site is less reactive, as in the case of low chain initiation rate constant, both the conversion and molecular weight of the polymer will be lowered.

In the built-in kinetics, chain transfer to hydrogen, cocatalysts, solvent, transfer agent, electron donor, monomer and spontaneous chain transfer are included as shown in Figure 4.14.

*Chain Transfer to Monomer*

For chain transfer to monomer a new polymer chain of unit length is generated while for the other transfer reactions a vacant site of that type is generated. The dead polymer chain formed by some of the chain transfer reactions will have an end-group with a terminal double bond. In addition to the rate constant parameters and the reaction order, the user may also specify a parameter to track the fraction of dead polymer chains with terminal double bonds that are generated from the chain transfer reactions. The default value for this parameter is zero.

## Site Deactivation

The catalyst site deactivation step involves the deactivation of active sites, vacant and propagation, to form dead sites. Depending on the catalyst system and operating conditions, the deactivation rate may be high or low.

There are several different site deactivations reactions included in the built-in kinetic scheme. They include site deactivation by cocatalyst, by electron donors, by hydrogen, by monomer, by poisons, and spontaneous site deactivation. Different catalyst systems tend to be deactivated by a different subset of the reactions.

The deactivation rate constants are assumed to be dependent only on the site type and not on the polymer segment attached to a site. Therefore, the same rate constant is applied to both vacant and propagation sites of the same type. Note that deactivation rates shown in Figure 4.14 are per unit of active (vacant and propagation) site concentration.

## Site Inhibition

Inhibited sites have small molecules such as hydrogen or poisons attached. As a result, inhibited sites are temporarily blocked from becoming propagation sites. The site inhibition reaction is considered reversible. Therefore, the small molecule may dissociate from an inhibited site which then becomes a vacant site once again. The user must specify rate constant parameters for both the forward (inhibition) and reverse (dissociation) reactions.

## Cocatalyst Poisoning

For some catalyst systems, additional amounts of cocatalysts are fed to the reactor to counteract the effect of any poisons present. This is modeled as a cocatalyst poisoning reaction in the built-in kinetics. The product of this reaction is designated as a byproduct in the list of reactive species. The byproduct is considered to be inert and does not participate in any reaction.

## Long Chain Branching Reactions

For some catalyst systems, primarily metallocene, polymer chains with long chain branches are formed. However, the long chain branching frequency is usually small. The long chain branches are believed to be due to propagation reactions involving a live chain and a terminal double bond on a dead polymer chain. Polymer chains with terminal double bonds are formed by some of the chain transfer reactions. To form long chain branches, the metal center must be open to provide a favorable reactivity ratio for the macromonomer.

# MODEL FEATURES AND ASSUMPTIONS

Following are the model features and assumptions used in the Ziegler-Natta polymerization model available in Polymers Plus.

## Phase Equilibria

The polymerization model is currently able to consider either a single phase system of vapor or liquid, or a two phase system consisting of vapor and liquid, in calculating concentrations for the reaction kinetics.

- For single phase systems, the reacting phase will be either vapor or liquid.
- For two phase systems, the liquid phase is assumed to be the reacting phase, and all the polymer is assumed to be in the liquid phase.

The phase equilibrium model will be extended in the future to include vapor-liquid-liquid phase equilibrium (VLLE).

## Rate Calculations

The Ziegler-Natta polymerization kinetic model supplies to the reactor models the reaction rates for the components and the rate of change of polymer attributes (e.g. the chain length distribution moments). The component reaction rates are computed from the kinetic scheme by summing over all reactions that involve the component. The site based moment rates are derived from a population balance and method of moments approach similar to that described in Section 4.2.

# POLYMER PROPERTIES CALCULATED

The following variables can be calculated by the built-in kinetics routine based on the polymer attributes selected, and the subset of the built-in kinetics used for a specific simulation:

- Zeroth, first and second moments for the composite and site based combined polymer
- Zeroth and first moments for the composite and site based live polymer
- Number and weight degree of polymerization and polydispersity index for the composite and site based bulk polymer (DPN, DPW, PDI and SDPN, SDPW, SPDI)
- Number and weight average molecular weight for the composite and site based bulk polymer (MWN, MWW and SMWN, SMWW)
- Copolymer segment composition for composite and site based bulk polymer (SFRAC and SSFRAC segment mole fractions)
- Total number long chain branches (LCB)
- Long chain branching frequencies (FLCB)
- Mole fraction of live bulk polymer chains (LPFRAC and LSPFRAC)
- Number average degree of polymerization for live polymer (LDPN and LSDPN)
- Copolymer segment composition for live polymer (LSFRAC and LSSFRAC)
- Live polymer active segment composition (LEFRAC and LSEFRAC)

These variables are stored as component attributes (See Chapter 2). It is assumed that attributes needed for the kinetic scheme are selected. The specification of the Ziegler-Natta Model is described later in this section.

In many cases, users may need to know polymer product properties related to the above structural properties. For example, users may be interested in melt flow rate or melt index, viscosity, density, etc. These properties can be calculated in user-supplied Fortran subroutines which take the polymer moments and structural information and return the desired property. An example use of a user supplied subroutine to return melt index is shown in the HDPE section of the *Polymers Plus Examples* & *Applications Case Book*.

# SPECIFYING ZIEGLER-NATTA POLYMERIZATION KINETICS

## Accessing the Ziegler-Natta Model

To access the Ziegler-Natta polymerization kinetic model:

1. From the Data Browser, find the **Reactions** folder.
2. From the **Reactions** folder, select **Reactions** again to get to the Reactions object manager.

   If the kinetic model already exists, double-click on the desired Reaction ID in the object manager or select **Edit** to get to the input forms.
3. To add a new model, from the **Reactions** object manager, select **New**. If necessary, change the default ID for the reaction.
4. Select Ziegler-Nat as the reaction type and click on **OK**.

## Specifying the Ziegler-Natta Model

The Ziegler-Natta model input forms are as listed below. Use these forms to define reacting species and enter reaction rate constant parameters.

| Use this sheet | To |
|---|---|
| Species | Define reacting species |
| Reactions | Specify reactions and rate constant parameters |
| Rate Constants | Summarize rate constant parameters |

## Specifying Reacting Species

You must specify the reacting species on the Species sheet:

1. In the **Polymer** field, specify the polymer produced.
2. In the **Monomers** field list the reacting monomers. For each monomer, in the **goes to** → field specify the polymer segment which the monomer converts to.
3. Continue listing other types of reacting species, e.g. solvents, transfer agents, etc.
4. Select the **Generate Reactions** option if you would like the reactions to be generated automatically.

   After going through the reaction generation once, it is recommended that you turn off this feature. Otherwise, the reaction generation will be performed repeatedly.

## Listing Reactions

The Ziegler-Natta model generates reactions based on the list of reacting species. You can view the system-generated reactions, then assign rate constant parameters to these reactions.

You can view a list of the system-generated reactions on the Reactions sheet. In the Reaction summary listing, for each reaction the first column indicates the reaction type. The second column lists the reactants, and the last column lists the products. The Data Browser window can be resized to better view the reaction listing. Use the following options:

| Click on | To |
|---|---|
| New | Add new reactions to the scheme |
| Edit | Edit the current reaction indicated by the row selector |
| Rate Constants | Specify reaction rate constant parameters for the reactions |

Click to select a reaction. Click a reaction then Control-Click to include additional reactions for multiple selection. Double-click to edit a reaction.

In addition, you may use the following buttons:

| Click on | To |
|---|---|
| Hide/Reveal  | Exclude/Include a reaction from the calculations |
| Delete  | Permanently remove a reaction from the model |

## Adding Reactions

To add a new reaction to the scheme, click on **New** to open the Add Reaction subform. When you open the Add Reaction subform:

1. In **Reaction type**, select a type for the new reaction.

   The **Reaction scheme** for that type is displayed.

2. In other reactant (e.g **Initiator**, **Catalyst**) fields enter the reactants of the categories allowed for that reaction type.

3. Click on **Cancel** to discard the new reaction

   – or –

   Click on **New** to add a new reaction

   – or –

   Click on N→ to check the **Completion status**

   – or –

   Click on **Done** to return to the reaction summary.

## Editing Reactions

To edit a reaction, click on **Edit** to open the Edit Reaction subform. When you open the Edit Reaction subform:

1. Modify the **Reaction type** as needed. The **Reaction scheme** for that type is displayed.

2. Modify reactants as needed.

3. Click on N→ to check the **Completion status**

   – or –

   Click on **Done** to return to the reaction summary.

## Assigning Rate Constants to Reactions

To assign rate constants to user reactions, click on **Rate Constants** to open the Rate Constant Parameters subform:

1. In the **Site No.** field, enter the site number.
2. In the **ko** field, enter the pre-exponential factor.
3. In the **Ea** field, enter the activation energy.
4. In the **Order** field, enter the order for component in reaction.
5. In the **Fraction** field, enter terminal double bond fraction.
6. In the **Tref** field, enter reference temperature.
7. Click on the stoichiometry list and select a new reaction to enter rate constants for another reaction. You can use the **Prev** and **Next** buttons to select the previous or next reaction in the list.
8. Click on the Summary tab to see a listing of all the rate constant parameters.
9. Click on  to check the **Completion status**

   – or –

   Click on **Close** to return to the reaction summary.

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# 4.5 IONIC POLYMERIZATION MODEL

This section covers the ionic polymerization kinetic model available in Polymers Plus. The cationic, anionic and group transfer addition polymerization kinetics can be modeled using this model.

Topics covered include:

- Summary of Applications
- Ionic Processes
- Reaction Kinetic Scheme
- Model Features and Assumptions
- Polymer Properties Calculated
- Specifying Ionic Polymerization Kinetics

# SUMMARY OF APPLICATIONS

Some examples of applicable polymers are given in below:

- Polystyrene - Anionic polymerization is used to produce narrow molecular weight distribution polystyrenes in small quantities. Cationic polymerization is used to produce low molecular weight polystyrenes for coatings and glues. Block copolymers of styrene and butadiene are produced commercially with anionic polymerization.
- Poly isobutylene - Low-to-medium molecular weight poly isobutylene is produced commercially by polymerization of high purity isobutylene in isobutane or hexane diluent using aluminum chloride or hexane trifluoride as a catalyst.
- Poly butene - Polybutenes are produced in solution by copolymerizing isobutylene and n-butene using aluminum chloride or hexane trifluoride as a catalyst.
- Poly butadiene - Block copolymers of styrene and butadiene are produced commercially with anionic polymerization.
- Polyoxides - Examples are poly ethylene oxide (PEO) and poly propylene oxide (PPO). Continuous tubular or column reactors or semibatch autoclaves are used. The polymerization can be carried out with different mechanisms: anionic (base catalysis), cationic (acid catalysis), or coordinate.

# IONIC PROCESSES

Many specialty polymers are manufactured by ionic polymerization processes. For the description of a specific ionic process, refer to the References section. Ionic polymers fall in the category of addition polymers, i.e., the reactive species grow in length by continuous addition of monomer units. However, there are several features that distinguish the ionic polymerization processes from other addition polymerization processes like free-radical and Ziegler-Natta:

1. Different propagating species are often present in ionic processes. These species may be free ions, tight ion pairs, loose ion pairs, dormant esters, etc. Moreover the propagating species are often in equilibrium.
2. Association or aggregation phenomena is common in BuLi type of initiators for anionic polymerization. The associated initiator is not reactive and is in equilibrium with its dissociated form. The association phenomena also takes place with growing polymer chains, which reduces the actual number of chains growing at any given time. This phenomena affects both the conversion and polymer properties.
3. Exchange reaction takes place between live and dormant polymer. The active species transfer from one polymer to another. This reaction controls the molecular weight distribution of the final polymer. If the exchange reaction rate constant >> propagation rate constant, then for increasing monomer conversion the polydispersity approaches a limiting value of 1.0.
4. Ionic reactions are a strong function of solvent, initiator and operating conditions and are susceptible to poisons.
5. Chain transfer and termination reactions may be negligible or absent in certain polymerization processes thus leading to formation of living polymers.

# REACTION KINETIC SCHEME

In the following sections, the general chemistry of ionic polymerization and the built-in initiator / polymerization kinetic scheme are described. The kinetic scheme is based on literature survey of ionic polymerization mechanisms. Ionic kinetic scheme can model either cationic, anionic or group-transfer polymerization. The ionic kinetic scheme in Polymers Plus is a super-set of all the above mentioned reactions.

*Reaction Steps*

There are a few key elementary reactions that apply to all ionic polymerization systems. These include the three basic reaction steps:

1. Formation of active species
2. Chain initiation
3. Propagation

There is almost no chain transfer in living polymerization. There are additional reactions for each chemistry which will be discussed later. There can be different forms of propagating species, e.g., free-ions, ion-pairs, and dormant esters. A given ionic polymerization system can have different combinations of these propagating species.

To account for different propagating species, the same framework is used as the Ziegler-Natta multi-site kinetics model. In the ionic model, each site refers to a unique type of active species. To model three propagating species for an initiator, the model will have three sites with each site corresponding to the unique propagating active species type. In this framework, the polymer produced by dormant esters will be stored in live polymer attributes for the selected dormant ester site.

*Polymer Molecules Tracked*

There are three different types of polymer molecules tracked by ionic kinetic scheme:

1. $P_{n,k}^{i}$ - live polymer molecule chains of length *n* with active segment *k* attached to the active center of type *i*.

   For example, free-ions can be site 1, ion-pairs as site 2 and dormant esters as site 3. The propagation rate constant for dormant esters ( $k_p$ for site 3) may be zero.

2. $Q_n^i$ - associated (or aggregate) polymer molecule chains of length *n* formed by association of propagating species of type *i*.

   The site based aggregate polymer attributes contain the information about polymer formed by association of different propagating species. For example, only the ion pairs propagating species may associate in case of BuLi type of initiators.

3. $D_n^i$ - dead polymer molecule chains of length *n* formed by active propagating species of type *i*.

The site based bulk polymer attributes contain information about the bulk polymer which is a sum of live, aggregate and dead polymer.

*Ionic Model Initiator Attributes*

The initiator in ionic model has three attributes which are solved along with moment equations:

$$P_0^i = \text{P0FLOW};\ P_0^{t,i} = \text{PT0FLOW};\ C_I^i = \text{CIONFLOW}$$

These variables are provided as attributes so that they can be used in user kinetics to add side reactions. For example, a transfer species $(P_0^{t,i})$ may undergo a side reaction with other components; addition of a salt with same counter ion $(C_I^i)$ may tilt the polymerization in one direction by allowing counter-ion to be in equilibrium with ion concentrations from other salts. The initiator decomposition reactions (involving $P_0^i$ or $I_m$) can also be modeled in Aspen Plus as user reactions which can be solved simultaneously with built-in ionic kinetics in Polymers Plus.

The built-in initiator and polymerization kinetic scheme is shown in Figure 4.15. The nomenclature used in the kinetic scheme is in Table 4.49. The ionic model is a terminal model, implying that the rate constants are functions of only terminal segment of the polymer chain.

*Reactive Species*

For copolymerization, the built-in kinetic scheme allows the user to specify the number of monomer types used. Similarly the user has the flexibility to specify the number of each type of reactive species present in the polymerization:

- Associated initiators
- Initiators
- Catalysts
- Exchange agents
- Chain transfer agents
- Termination agents

The user is able to tailor the built-in kinetics to model a specific polymerization system by selecting a subset of the reactions shown in Figure 4.15.

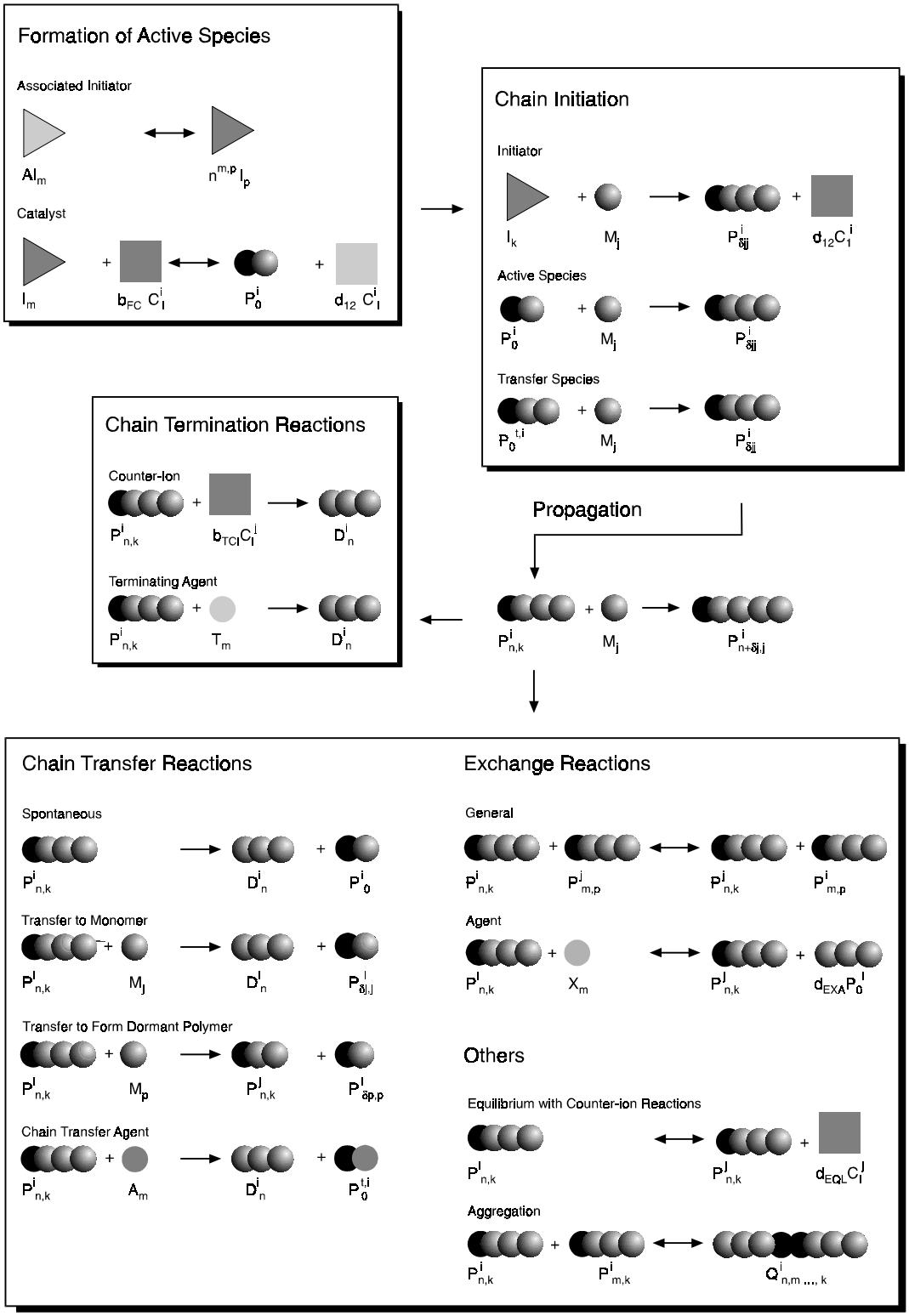


***Figure 4.15*** *Built-In Ionic Polymerization Kinetic Scheme*

### Table 4.49 Ionic Polymerization Kinetics Nomenclature

| Symbol | Description |
|---|---|
| $A_m$ | Chain transfer agent, m |
| $AI_m$ | Associated initiator, m |
| $b_{FC}$ | Coefficient (= 0 when catalyst does not participate in the reaction) |
| $b_{TCI}$ | Coefficient (= 0 when C-ion does not participate in the reaction) |
| $C_I^i$ | Counter ion (C-ion) corresponding to active species of type i |
| $C_n$ | Catalyst, n |
| $D_n^i$ | Dead polymer chain length of n produced by active species of type i |
| $d_{EQL}$ | Coefficient (= 0 when C-ion does not participate in the reaction) |
| $d_{EXA}$ | Coefficient (= 0 when Po does not participate in the reaction) |
| $d_{FC}$ | Coefficient (= 0 when C-ion does not participate in the reaction) |
| $d_{I2}$ | Coefficient (= 0 when C-ion is not formed in the reaction) |
| $I_p$ | Initiator, p |
| $M_j$ | Monomer, j |
| $n^{m,p}$ | Association number for initiator dissociation reaction |
| $P_0^i$ | Active species of type i (chain length 0) |
| $P_0^{t,i}$ | Transfer active species of type i (chain length 0) |
| $P^i_{\delta j,j}$ | Active species of type i with active segment j (chain length 1) |
| $P_{n,k}^i$ | Growing species chain of length n of type i with active segment k |
| $Q_{n,k}^i$ | Associated polymeric species of chain length n with active segment k |
| $T_m$ | Terminating agent, m |
| $X_m$ | Exchange agent, m |

The rate constants for each reaction for active species of type *i* are calculated at the reaction temperature using the Arrhenius equation shown below. The user specified rate constant parameters are pre-exponential factor $(k_o^i)$ and the activation energy $(Ea^i)$ at active species of type *i:*

*Rate Constant*

$$k^i = k_o^i \exp\left(-\frac{Ea^i}{R}\left(\frac{1}{T}-\frac{1}{T_{ref}}\right)\right)$$

Where:

$k_o$ = pre-exponential factor in 1/sec for first order reactions and $m^3 / kmol - \sec$ for second order reactions

$Ea$ = activation energy in mole enthalpy units

$R$ = universal constant

$T$ = reaction temperature in Kelvin

$T_{ref}$ = reference reaction temperature in Kelvin (default is 1E38)

## Formation of Active Species

The active species is the initiator in dissociated form:

$$AI_m \Leftrightarrow n^{m,p}\ I_p$$

The association and dissociation of initiator is observed in alkyl-Lithium type of initiators in nonpolar solvents for anionic polymerization. n-butyl-Li exists as hexamer whereas s-BuLi and t-BuLi exist as tetramers for styrene polymerization. The dissociated initiator further reacts with monomer to form growing polymer with unit chain length in chain initiation step. This reaction can also be used to represent self-ionization of some strong acids $(AlCl_3,\ AlBr_3,\ TiCl_3)$ in cationic polymerization, with $n^{m,p}$ being the degree of ionization:

$$I_m + b_{FC}\ C_n \ \Leftrightarrow\ P_0^i + d_{FC}\ C_I^i$$

The active species $P_0^i$ is formed by this reaction. Several initiators $(KNH_2,\ NaNH_2)$ decompose to form an active species (or dissociate into ions) in anionic polymerization $(b_{FC} = 0,\quad d_{FC} = 1)$. Polystyrene is manufactured using $KNH_2$ initiator.

With no reverse reaction, the electron transfer initiation with light (electrochemical initiation) is also a special case of the above scheme for anionic polymerization. Initiator and catalyst are used in cationic polymerization with no counter-ion $(d_{FC} = 0)$. In case of anionic polymerization, a starter may be used to generate an active species.

For polyether polyols (polypropylene oxide), initiator is ROH and catalyst is KOH (weak base) and the reaction is only in forward direction.

The above scheme can also represent donar-accepter equilibria and self dissociation of acids in cationic initiation $(A+B \Leftrightarrow A^{-}+B^{+})$.

## Chain Initiation Reactions

The active species incorporate monomer to form propagating species with unit chain length:

$$P_0^i + M_j \rightarrow P^i_{\delta j,j}$$

The initiator (in dissociated form) directly reacts with monomer to form propagating species with unit chain length. A counter-ion may be formed $(d_{I2} = 1)$:

$$I_m + M_j \rightarrow P^i_{\delta j,j} + d_{I2}\, C_I^i$$

The transfer active species incorporate monomer to form propagating species with unit chain length:

$$P_0^{t,i} + M_j \rightarrow P^i_{\delta j,j}$$

## Propagation Reaction

The growing polymer with an active species at the end of the chain may grow or propagate through the addition of monomer molecules to form long polymer chains. The propagation reaction is represented by:

$$P^i_{n,k} + M_j \rightarrow P^i_{n+\delta j,\, j}$$

where monomer *j* is being added to a polymer chain of length *n*, with an active segment of type *k* and active species of type *i*. The resulting polymer chain will be of length *n*+1 and the active segment will be of type *j*. The active segment type usually represents the last monomer type incorporated into the polymer chain.

*Copolymerization Reaction Rates*

For copolymerization, there will be $N_m * N_m * N_{site}$ propagation reactions that may have different reactivities. For example, with two monomers and three site types, the monomer being added could be monomer 1 or monomer 2 while the active segment type could be segments from monomer 1 or monomer 2 at each site type. As a result, there will be twelve rate constants $(k^i_{p,kj})$, where the subscript *k* refers to the active segment type while the second subscript *j* refers to the propagating monomer type. The superscript *i* refers to active species type.

For the terminal model the rate of propagation is dependent only on the concentration of live polymer with active segment *k* on active species *i* and the concentration of the propagating monomer *j*.

## Association or Aggregation Reaction

The propagating species initiated by alkyl-Lithium type of initiators in anionic polymerization also exhibit the association phenomena like the initiator. The association of live polymeric species is usually dimeric in nature. The associated polymer $Q^i_{n+m,\,k}$ is tracked as a separate polymer and does not participate in any other reactions:

$$P^i_{n,\,k} + P^i_{m,\,k} \Leftrightarrow Q^i_{n+m,k}$$

## Exchange Reactions

Exchange reactions exchange the growing active species between two different growing polymers. If both free ions and ion pairs are growing, then the counter-ion can exchange between the two polymeric species. There can be exchange reaction between dormant polymer (with ester as growing species which does not propagate) and ion pairs/free ions. The exchange reaction can also take place between an exchange agent (e.g., alcohol end group in solvent or starter) and a growing polymer. If exchange reaction with a small molecule does not produce a $P_0$ species, then $d_{EXA} = 0$. The exchange between growing species and dormant species takes place in polyether polyols (propylene oxide). The dormant species can be an alcohol:

$$P^i_{n,k} + P^j_{m,p} \Leftrightarrow P^j_{n,k} + P^i_{m,p}$$

$$P^i_{n,k} + X_m \Leftrightarrow P^j_{n,k} + d_{EXA}\, P^i_0$$

## Equilibrium with Counter-Ion Reactions

The following reaction represents the equilibrium between free ions and ion pairs, hence the name equilibrium with counter-ion $(d_{EQL} = 1)$. The spontaneous ionization reaction can also be represented by this reaction when $d_{EQL} = 0$:

$$P^i_{n,k} \Leftrightarrow P^j_{n,k} + d_{EQL}\, C^j_I$$

## Chain Transfer Reactions

There are four types of chain transfer reactions:

- Spontaneous
- Monomer
- Dormant polymer formation
- Chain transfer agent

Spontaneous chain transfer can lead to formation of a dead polymer molecule and an active species caused by proton loss, e.g., cationic polymerization of poly isobutylene:

Spontaneous $$P^i_{n,k} \rightarrow D^i_n + P^i_0$$

Chain transfer to monomer can take place with hydride abstraction from an olefin, for example, cationic polymerization of polyisobutylene and butyl rubber:

Monomer $$P^i_{n,k} + M_j \rightarrow D^i_n + P^i_{\delta j,j}$$

Chain transfer to monomer in polyethers (propylene oxide) can form dormant species (alcohol). The dormant species is modeled as a live polymer with a different site type but it does not have the usual chain initiation and propagation reactions. This dormant polymer can participate in exchange reactions:

Form dormant polymer $$P^i_{n,k} + M_p \rightarrow P^j_{n,k} + P^i_{\delta p,p}$$

The growing polymer chain can also be transferred to a chain transfer agent, *A*, leading to formation of a transfer active species of the same type, *i*. The reaction rate order *wrt*. to chain transfer agent can be specified by the user:

Chain transfer agent $$P^i_{n,k} + A_m \rightarrow D^i_n + P^{t,i}_0$$

## Chain Termination Reactions

The growing polymer chain with ion pairs as active species can be spontaneously terminated by combination with counter ion $(b_{TCI} = 0)$, e.g., cationic polymerization of polystyrene, tetrahydrofuran, polyisobutylene. A growing free ion active species can terminate by reacting with its own counter ion $(b_{TCI} = 1)$:

Counter-ion $$P^i_{n,k} + b_{TCI} C^i_I \rightarrow D^i_n$$

The chain can terminate after reacting with a chain terminating agent to form a dead polymer. Any small molecule can act as a chain terminating agent. The reaction rate order *wrt*. to terminating agent can be specified by the user:

Terminating agent $$P^i_{n,k} + T_m \rightarrow D^i_n$$

# MODEL FEATURES AND ASSUMPTIONS

Following are the model features and assumptions used in the ionic polymerization model available in Polymers Plus.

## Phase Equilibria

The polymerization model is currently able to consider either a single phase system of vapor or liquid, or a two phase system consisting of vapor and liquid, in calculating concentrations for the reaction kinetics. For single phase systems, the reacting phase will be either vapor or liquid. For two phase systems, the liquid phase is assumed to be the reacting phase, and all the polymer is assumed to be in the liquid phase. The phase equilibrium model will be extended in the future to include vapor-liquid-liquid phase equilibrium (VLLE).

## Rate Calculations

The ionic polymerization kinetic model supplies to the reactor models the reaction rates for the components and the rate of change of polymer attributes (e.g. the chain length distribution moments):

- The component reaction rates are computed from the kinetic scheme by summing over all reactions that involve the component.
- The site based moment rates are derived from a population balance and method of moments approach similar to that described in the free-radical section (Section 4.2).

Additionally, the moment definitions are modified to include the aggregate polymer as separate and as a part of bulk polymer. The attributes calculate and report up to third moments of live, aggregate and bulk polymer. Table 4.50 shows the moment definitions.

***Table 4.50 Fth Order Moment Definition***

| Polymer | | Moment Definition |
|---|---|---|
| Live Polymer | $P_{n,k}^{i}$ | $\mu_{f,k}^{i} = \sum_{n}^{\infty} n^{f} P_{n,k}^{i}$ |
| Aggregate Polymer | $Q_{n,k}^{i}$ | $\xi_{f,k}^{i} = \sum_{n}^{\infty} n^{f} Q_{n,k}^{i}$ |
| Dissociated Aggregate Polymer | $Q_{n+m,k}^{i}$ | $\eta_{f,k}^{i} = \sum_{n}^{\infty} n^{f} \sum_{m}^{\infty} Q_{n+m,k}^{i}$ |
| Bulk Polymer | | $\lambda_{f}^{i} = \sum_{k}^{\infty} n^{f} \left[ \sum_{k}^{Nseg} \left\{ P_{n,k}^{i} + Q_{n,k}^{i} \right\} + D_{n}^{i} \right]$ $= \sum_{k}^{Nseg} \mu_{f,k}^{i} + \sum_{k}^{Nseg} \xi_{f,k}^{i} + \sum_{n}^{\infty} n^{f} D_{n}^{i}$ |

# POLYMER PROPERTIES CALCULATED

The following variables can be calculated by the built-in kinetics routine based on the polymer attributes selected, and the subset of the built-in kinetics used for a specific simulation:

- Zeroth, first and second moments for the composite and site based bulk polymer
- Zeroth and first moments for the composite and site based live polymer and aggregate polymer
- Number and weight degree of polymerization and polydispersity index for the composite and site based bulk polymer (DPN, DPW, PDI and SDPN, SDPW, SPDI)
- Number and weight average molecular weight for the composite and site based bulk polymer (MWN, MWW and SMWN, SMWW)
- Copolymer segment composition for composite and site based bulk polymer (SFRAC and SSFRAC segment mole fractions)
- Mole fraction of bulk polymer chains that are live (LPFRAC and LSPFRAC)
- Mole fraction of bulk polymer chains that are aggregated (APFRAC and ASPFRAC)
- Number average degree of polymerization for live polymer (LDPN and LSDPN)
- Number and weight average degree of polymerization for aggregate polymer (ADPN, ADPW, ASDPN and ASDPW)

- Copolymer segment composition for live and aggregate polymer (LSFRAC, ASFRAC, LSSFRAC and ASSFRAC)
- Live polymer active segment composition (LEFRAC and LSEFRAC)

These variables are stored as component attributes. See Chapter 2 for a description of these component attributes. It is assumed here that attributes needed for the kinetic scheme are selected. For each live polymer attribute, there is also a corresponding aggregate polymer attribute.

# SPECIFYING IONIC POLYMERIZATION KINETICS

## Accessing the Ionic Model

To access the Ionic polymerization kinetic model:

1. From the Data Browser, find the **Reactions** folder.
2. From the **Reactions** folder, select **Reactions** again to get to the Reactions object manager.

   If the kinetic model already exists, double-click on the desired Reaction ID in the object manager or select **Edit** to get to the input forms.
3. To add a new model, from the **Reactions** object manager, select **New**. If necessary, change the default ID for the reaction.
4. Select Ionic as the reaction type and click on **OK**.

## Specifying the Ionic Model

The Ionic model input forms are as listed below. Use these forms to define reacting species and enter reaction rate constant parameters:

| Use this sheet | To |
|---|---|
| Species | Define reacting species |
| Reactions | Specify reactions and rate constant parameters |
| Rate Constants | Summarize rate constant parameters |

## Specifying Reacting Species

You must specify the reacting species on the Species sheet:

1. In the **Polymer** field, specify the polymer produced.
2. In the **Monomers** field list the reacting monomers.

   For each monomer, in the **goes to** → field specify the polymer segment which the monomer converts to.
3. Continue listing other types of reacting species, e.g. solvents, transfer agents, etc.

## Listing Reactions

You can build a list of reactions on the Reactions sheet. In the Reaction summary listing, for each reaction the first column indicates the reaction type. The second column lists the reactants, and the last column lists the products. The Data Browser window can be resized to better view the reaction listing. Use the following options:

| Click on | To |
|---|---|
| New | Add new reactions to the scheme |
| Edit | Edit the current reaction indicated by the row selector |
| Rate Constants | Specify reaction rate constant parameters for the reactions |

Click to select a reaction. Click a reaction then Control-Click to include additional reactions for multiple selection. Double-click to edit a reaction.

In addition, you may use the following buttons:

| Click on | | To |
|---|---|---|
| Hide/Reveal |  | Exclude/Include a reaction from the calculations |
| Delete |  | Permanently remove a reaction from the model |

## Adding Reactions

To add a new reaction to the scheme, click on **New** to open the Add Reaction subform. When you open the Add Reaction subform:

1. In **Reaction type**, select a type for the new reaction. The **Reaction scheme** for that type is displayed.
2. In other reactant (e.g **Initiator**, **Catalyst**) fields enter the reactants of the categories allowed for that reaction type.
3. Click on **Cancel** to discard the new reaction

   – or –

   Click on **New** to add a new reaction

   – or –

   Click on  to check the **Completion status**

   – or –

   Click on **Done** to return to the reaction summary.

## Editing Reactions

To add or edit a reaction, click on **Edit** to open the Edit Reaction subform. When you open the Edit Reaction subform:

1. Modify the **Reaction type** as needed.

   The **Reaction scheme** for that type is displayed.
2. Modify reactants as needed.
3. Click on  to check the **Completion status**

   – or –

   Click on **Done** to return to the reaction summary.

## Assigning Rate Constants to Reactions

To assign rate constants to user reactions, click on **Rate Constants** to open the Rate Constant Parameters subform:

1. In the **ko(fwd)** or **(rev)** field, enter the pre-exponential factor for forward or reverse reaction.
2. In the **Ea(fwd)** or **(rev)** field, enter the activation energy for forward or reverse reaction.
3. In the **Tref** field, enter reference temperature.
4. In the **Order** field, enter the order.
5. In the **Asso. No.** field, enter the polymer association number.
6. In the **Coeff. b** and **Coeff. d** fields, enter coefficients b and d.
7. Click on the stoichiometry list and select a new reaction to enter rate constants for another reaction. You can use the **Prev** and **Next** buttons to select the previous or next reaction in the list.
8. Click on the Summary tab to see a listing of all the rate constant parameters.
9. Click on  to check the **Completion status**

   – or –

   Click on **Close** to return to the reaction summary.

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# 4.6 SEGMENT-BASED REACTION MODEL

This section describes the segment-based polymer modification reaction model available in Polymers Plus.

Topics covered include:

- Summary of Applications
- Polymer Modification Processes
- Segment-Based Model Allowed Reactions
- Model Features and Assumptions
- Polymer Properties Calculated
- Specifying Segment-Based Polymer Modification Reactions

## SUMMARY OF APPLICATIONS

This model may be used to represent processes involving changes to polymer segments. The underlying kinetics are basic power law reactions in which segments and monomeric components may participate. Some examples of applicable polymers are:

- Polyvinyl alcohol (PVA) - Alcoholysis of polyvinylacetate
- Chlorinated polyethylene (CPE) - Chlorination of polyethylene
- Polymethylmethacrylate (PMMA) - Recovery of methylmethacrylate from PMMA
- Polyisobutylene - Chain scission of polyisobutylene

# POLYMER MODIFICATION PROCESSES

The conventional route for synthesizing commercial polymers is through the polymerization of a monomeric compound. These polymerization reactions fall under different categories depending on the nature of the monomer and its growth mechanism.

However, once synthesized, polymers may undergo further reactions. In some instances, these reactions may be undesirable side reactions, in which case they may be considered as degradation reactions. In other cases, the only mechanism for producing certain polymers may be through the modification of a starting polymer. Typically, this situation occurs if a monomer is not readily available for that polymer. For example, polyvinyl alcohol is produced by alcoholysis of polyvinyl acetate.

In addition, modification reactions are often used to improve polymer properties such as oil resistance (chlorosulfonation of polyethylene), heat resistance (chlorination of polyethylene), solubility ("-cellulose), and flammability (natural rubber). There are also a few cases where it is economically desirable to react scrap polymer for monomer recovery (methyl methacrylate from polymethyl methacrylate) (Rodriguez, 1989).

*Reaction Categories*

Regardless of the end effect of the polymer modification reaction, the events taking place fall into one of two categories based on the site where they occur on the polymer chain. The reactions may take place on:

- Side groups
- Polymer backbone: scission, depolymerization, cross-linking, or bond changes

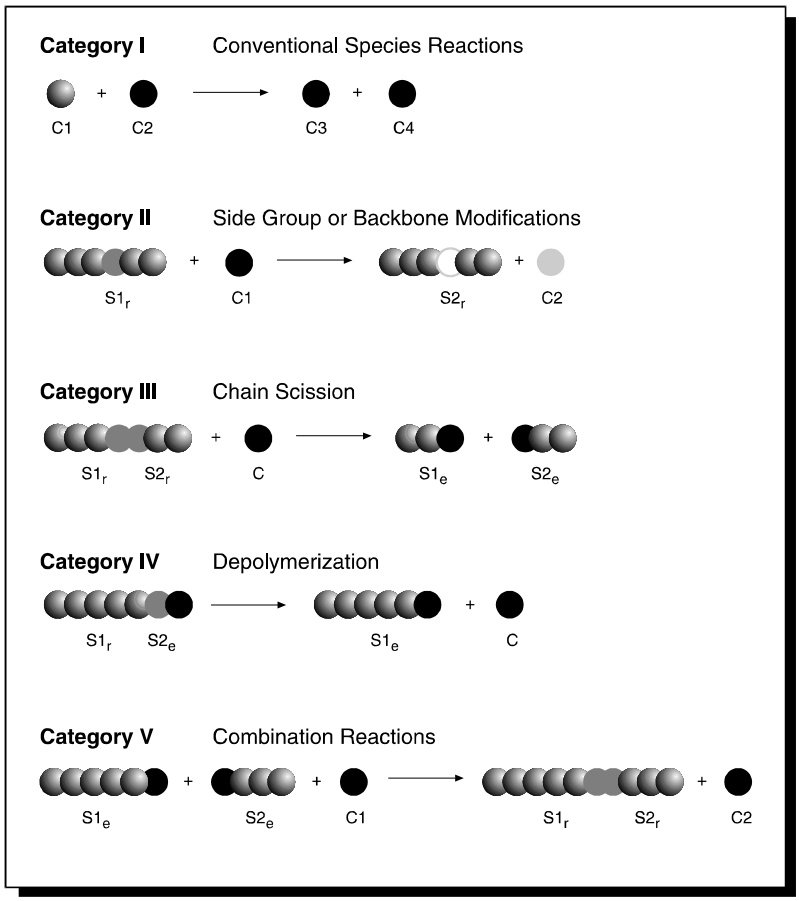
In addition, there are some fundamental issues that distinguish reacting polymers from their low molecular weight counterparts. One obvious characteristic of reacting polymers is the potential for steric hindrance. A reacting side group may be too close to the polymer chain, for example. There may also be changes in solubility as reaction progresses.

Furthermore, crystallinity has an effect on the polymer reactivity; in general, for a semicrystalline polymer, only the amorphous region is able to react.

Finally, an important difference that characterizes polymers is the fact that a higher local concentration of reacting functional groups is observed than that indicated by the overall polymer concentration (Odian, 1991).

# SEGMENT-BASED MODEL ALLOWED REACTIONS

The reaction categories allowed in the segment-based reaction model are summarized in Figure 4.16. A brief summary of the conditions where each of these reactions may occur is also given.




**Notes**

C represents a conventional component, S represents a segment, the subscripts r and e represent units and groups respectively.

Stoichiometric coefficients have been omitted in above notation for the sake of simplicity. The model does however enforce material balance for each equation category.

Category II reactions are valid for any segment type provided that both reactant segment and product segment are of the same type.

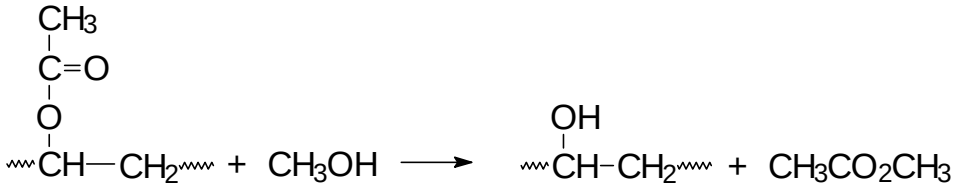
***Figure 4.16*** *Segment Based Model Reaction Categories*

## Conventional Species Reactions

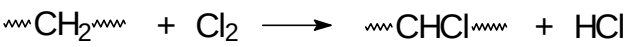
Reactions involving all non polymeric species fall under this category. As part of the polymer modification reaction scheme, monomeric components present may react among themselves to produce intermediate species. These reactions are represented as Category I in Figure 4.16.

## Side Group or Backbone Modifications

Polymer modification reactions aimed at altering end properties involve in most cases side group or backbone modifications. In such reactions, groups attached to the polymer chain are substituted. One example is that of the alcoholysis of polyvinyl acetate to produce polyvinyl alcohol:



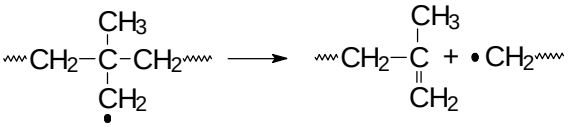
Another example is the chlorination of polyethylene to produce chlorinated polyethylene (CPE):



Side group and backbone reactions are illustrated as reaction Category II in Figure 4.16.

## Chain Scission

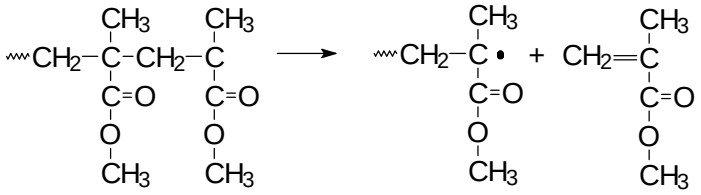
A common polymer degradation reaction is chain scission. In this case, bonds are broken along the polymer chain resulting in shorter polymer molecules with lower molecular weight. Chain scission may be induced by several factors. One example is the scission of polyisobutylene upon oxidation:



Chain scission reactions are represented as Category III reactions in Figure 4.16.

## De-polymerization

Depolymerization is the reverse of the propagation step of a polymerization reaction. In such reactions, monomer molecules are lost from the polymer chain. Depolymerization is often considered a degradation reaction. There are, however, cases where it is brought on by design to recover monomer from scrap polymer. An example depolymerization reaction is that of polymethyl methacrylate to regenerate methyl methacrylate:



Depolymerization is illustrated as Category IV in Figure 4.16.

## Combination Reactions

There are other mechanisms through which polymer segments react with each other. Some of these reactions, grouped as combination reactions, include kinetic events where two polymer molecules combine into one. These reactions are represented as Category V in Figure 4.16. Other reaction categories not listed include addition reactions to which specific kinetic models are devoted, and cross-linking reactions.

## Kinetic Rate Expression

The segment-based reaction model follows the power-law rate expression where the rate of reaction is calculated as the product of the reacting species concentrations with a rate constant representing the specific reactivity of the reaction. The kinetic rate expression in the segment-based model is described below:

$$rate = \left(\prod_j C_j^{\alpha_{ij}}\right) k_{oi} e^{\frac{-Ea_i}{R}\left(\frac{1}{T}-\frac{1}{T_{ref}}\right)} \qquad \textbf{(4.48)}$$

Where:

| | | |
|---|---|---|
| $i$ | = | user reaction number |
| $j$ | = | component number |
| $\Pi$ | = | product operator |
| $C_j$ | = | concentration of component $j$ |
| $\alpha_{ij}$ | = | power law exponent for component $j$ in reaction $i$ |
| $k_o$ | = | preexponential factor |
| $Ea$ | = | activation energy (Mole-Enthalpy units) |
| $b$ | = | temperature exponent |
| $R$ | = | universal gas constant |
| $T$ | = | temperature (Temperature units) |
| $T_{ref}$ | = | optional reference temperature (Temperature units) |

*Polymer Mole Fraction Conversion to Segment Mole Fraction*

Component concentrations depend on the calculation basis: molarity, mole fraction, mass fraction, mass concentration, etc. The polymer mole fraction is converted into its segment mole fractions according to the following equation:

$$Frac_{s,i} = Frac_p * SFRAC(i) * \frac{Mw_p}{Mwseg_{avg}} \qquad \textbf{(4.49)}$$

Where:

| | | |
|---|---|---|
| $Frac_{s,i}$ | = | segment mole fraction |
| $SFRAC(i)$ | = | polymer segment fraction (component attribute) |
| $Mw_p$ | = | polymer molecular weight |
| $Mwseg_{avg}$ | = | average segment molecular weight = $\sum_1^{Nseg} SFRAC(i) * Mw_i$ |

# MODEL FEATURES AND ASSUMPTIONS

The following assumptions are built into the segment-based reaction model:

- Reactions may occur either in the backbone or on the surface of the polymer
- Mass balance holds for components involved in the reactions on segment basis
- Moment of chain length distribution calculations cover up to the first moment
- Since higher moments not covered, segment-based model should be last in reaction block sequencing

# POLYMER PROPERTIES CALCULATED

The segment-based reaction model calculates and returns the following information:

- Rate of change for all components involved in reaction scheme, and rate of change for all segments
- Polymer segment composition
- Zeroth moment of chain length distribution
- First moment of chain length distribution

This information is returned through the stream compositions for the component rate of change, and through the polymer component attributes for the segment rate of change and moment calculations.

The rate of change of polymer mass is calculated as follows:

$$R_p = \frac{\sum_{1}^{Nseg} R_{s,i} * Mw_i}{Mw_p} \qquad \textbf{(4.50)}$$

This is the sum of the rates of change of segment masses.

# SPECIFYING SEGMENT-BASED POLYMER MODIFICATION REACTIONS

## Accessing the Segment-Based Model

To access the Segment-Based polymerization kinetic model:

1. From the Data Browser, find the **Reactions** folder.
2. From the **Reactions** folder, select **Reactions** again to get to the Reactions object manager.

   If the kinetic model already exists, double-click on the desired Reaction ID in the object manager or select **Edit** to get to the input forms.
3. To add a new model, from the **Reactions** object manager, select **New**. If necessary, change the default ID for the reaction.
4. Select Segment-Bas as the reaction type and click on **OK**.

## Specifying the Segment-Based Model

The Segment-Based model input forms are as listed below. Use these forms to specify reaction conditions and build a reaction scheme.

| Use this sheet | To |
|---|---|
| Specs | Define reacting phase, concentration basis, and reacting polymer |
| Reactions | Define reaction stoichiomerty and enter reaction rate constant parameters |

## Specifying Reaction Settings

Use the Specs sheet to define the reaction model settings:

1. In the **Reacting polymer** field, specify the reacting polymer.
2. In the **Reference temperature** field, specify the reference temperature for rate constant parameters.
3. In the **Phase** field, specify the phase in which reactions occur.
4. In the **Basis** field, specify the basis for component concentrations in the reaction rate calculation.

## Building a Reaction Scheme

You can build a list of reactions on the Reactions sheet. To do this you must specify a reaction stoichiometry and the associated rate constants. The Data Browser window can be resized to better view the reaction listing. Use the following options:

| Click on | To |
|---|---|
| New | Add new reactions to the scheme |
| Edit | Edit the current reaction indicated by the row selector |
| Rate Constants | Specify reaction rate constant parameters for the reactions |

Click to select a reaction. Click a reaction then Control-Click to include additional reactions for multiple selection. Double-click to edit a reaction.

In addition, you may use the following buttons:

| Click on | To |
|---|---|
| Hide/Reveal  | Exclude/Include a reaction from the calculations |
| Delete  | Permanently remove a reaction from the model |

## Adding or Editing Reactions

To add a new reaction to the scheme or to edit an existing reaction, click on **New** or **Edit** to open the Edit Stoichiometry subform:

Note that in the **Reaction no.** field, a unique number is assigned to the reaction being added.

1. Specify the **Component ID** and stoichiometric **Coefficient** for the reactants. Reactants must have a negative coefficient.
2. Specify the **Component ID** and stoichiometric **Coefficient** for the products. Products must have a positive coefficient.
3. Click on N> to check the **Completion status**

   – or –

   Click **Close** to return to the reaction summary.

## Assigning Rate Constants to Reactions

To assign rate constants to user reactions, click on **Rate Constants** to open the Rate Constant Parameters subform:

1. In the $k_o$ field, enter the pre-exponential factor.
2. In the $E_a$ field, enter the activation energy.
3. In the **b** field, enter the temperature exponent for temperature in Kelvin.
4. In the $T_{ref}$ field, enter the reference temperature.
5. In the **Basis** field, enter basis as Mole concentration.
6. Specify the power-law exponents.
7. Click on the stoichiometry list and select a new reaction to enter rate constants for another reaction.
8. Click on N> to check the **Completion status**

   – or –

   Click on **Close** to return to the reaction summary.

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