



## Newly Applied Two-Dimensional Solid-State NMR Correlation Techniques for the Characterization of Organically Modified Silicates

F. BABONNEAU,\* V. GUALANDRIS AND J. MAQUET

*Chimie de la Matière Condensée, UPMC/CNRS, 4 Place Jussieu 75005 Paris, France*

fb@ccr.jussieu.fr

D. MASSIOT

*CNRS-CRMHT, 45071 Orléans Cedex 2, France*

M.T. JANICKE AND B.F. CHMELKA

*Dept. of Chemical Engineering, University of California Santa Barbara, CA 93106, USA*

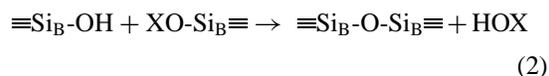
**Abstract.** This paper highlights the use of two-dimensional (2D) solid-state NMR correlation techniques to probe the chemical homogeneity of organically modified silicate networks. Specifically,  $^{29}\text{Si}\{^1\text{H}\}$  heteronuclear correlation (HETCOR) NMR experiments have revealed the spatial proximity of the two types of Si units present in a gel obtained from co-hydrolysis of methyldiethoxysilane and triethoxysilane. Similar information has also been obtained by using 2D  $^1\text{H}$  homonuclear correlation NMR spectroscopy. Such experiments were only possible by combining the use of high magnetic field (14.10 T) with fast MAS spinning rate (30 kHz).

**Keywords:** hybrid systems, polysiloxanes, structure, solid state NMR

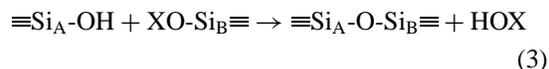
### 1. Introduction

Hydrolysis and condensation of organosilanes generally lead to the formation of organically modified silicate networks in which organic R groups are directly grafted to the silicate network [1]. The spatial distribution of the various constitutive units in the final gel network depends on the chemical reactivity of the starting monomeric precursors whose hydrolytic reactivities may be different [2]. Both self-condensation (1) and co-condensation (2, 3) reactions can occur, and this will influence the nature of the condensed species formed in solution.

Self-condensation:



Co-condensation:



Complex series of often competitive chemical reactions are present at each stage of the synthesis procedure, not only in solution (hydrolysis and condensation), but also during aging before gelation, and then during drying. They will strongly influence the process of network formation, and consequently the structural properties of the final materials. It is thus important to use appropriate characterization tools not only to identify and quantify the building units, but also to probe their spatial arrangements.

In these organically modified silicates, the presence of protonated groups that are directly bonded to some

\*To whom all correspondence should be addressed.

Si atoms makes the use of  $^{29}\text{Si}\{^1\text{H}\}$  cross-polarization (CP) technique very valuable. Based on magnetization transfer between abundant and rare spins (here  $^1\text{H}$  and  $^{29}\text{Si}$  respectively), this technique has been often combined with MAS and high power proton decoupling to increase the sensitivity of dilute nuclei [3]. The efficiency of magnetization transfer, which occurs during the contact time  $t_c$ , is directly related to the  $^{29}\text{Si}\text{-}^1\text{H}$  dipolar coupling strength and thus to the  $^{29}\text{Si}\text{-}^1\text{H}$  distances and mobility. Study of the polarization transfer dynamics can thus provide structural information about the proton environment of each detected Si sites.

But, the main difficulty encountered in the one-dimensional (1D) CP experiment is the uncertain nature of the protons that are the actual sources of the magnetization that is transferred, which interferes with conclusions concerning the spatial proximities between  $^1\text{H}$  and  $^{29}\text{Si}$  nuclei. The use of two-dimensional (2D)  $^{29}\text{Si}\{^1\text{H}\}$  CP-MAS heteronuclear (HETCOR) NMR experiment can, however, circumvent this problem. This technique was first introduced to characterize surface species on silica and zeolite [4] and has also been applied to two siloxane-silica systems prepared from methyltriethoxysilane (MTES) and tetraethoxysilane (TEOS) [5] and phenyltriethoxysilane (PhTES) and tetraethoxysilane (TEOS) [6]. In these examples, only one contact time,  $t_c$ , was used for each system. But, indeed,  $t_c$  can be used as a parameter to probe the spatial proximity between the protons and the various  $^{29}\text{Si}$  sites.

This paper will present results obtained with 2D  $^{29}\text{Si}\{^1\text{H}\}$  HETCOR MAS NMR experiments, as well as 2D  $^1\text{H}$  homonuclear correlation MAS NMR experiments, to probe the chemical homogeneity of hybrid networks prepared by co-hydrolysis of methyldiethoxysilane and triethoxysilane.

## 2. Experimental

All chemicals have been used as received. The gel was prepared by co-hydrolyzing methyldiethoxysilane ( $(\text{CH}_3)_2\text{HSi}(\text{OEt})_2$ ) and triethoxysilane  $\text{HSi}(\text{OEt})_3$  in a 1/1 ratio under acidic conditions ( $\text{EtOH}/\text{Si} = 2$ ;  $\text{H}_2\text{O}/\text{OEt} = 1$ ;  $\text{pH} = 2(\text{HCl})$ ). The resulting solution was aged in closed tubes at  $60^\circ\text{C}$  for 24 h, during which gelation occurred. Then, the gel was dried at  $100^\circ\text{C}$  for several days. The notation  $\text{T}^{\text{H}}$  and  $\text{D}^{\text{H}}$  will be used respectively for the  $\text{CH}_3\text{HSiO}_2$  and  $\text{HSiO}_3$  sites and the gel will be labeled  $\text{T}^{\text{H}}\text{D}^{\text{H}}1$ .

The 2D  $^{29}\text{Si}\{^1\text{H}\}$  heteronuclear correlation MAS-NMR experiments were recorded on a Bruker

MSL-300 spectrometer (7.05 T) and a Chemagnetics CMX-500 spectrometer (11.75 T). TPPI was used for phase sensitivity with a 3-s repetition time and 128 individual experiments with 8 to 48 acquisitions. The  $^1\text{H}$  MAS-NMR experiments were recorded on a Bruker DRX600 spectrometer (14.10 T) equipped with a high-speed MAS probe-head (2.5 mm zirconia rotors), capable of spinning up to 35 kHz. The 1D  $^1\text{H}$  spectra were recorded with 125-kHz spectral width, 1-s recycle delay and 2.75- $\mu\text{s}$   $90^\circ$  pulses. For the 2D experiments, 16 acquisitions with a 10-kHz spectral width and 2-s delay were recorded for each of the 128  $t_1$  experiments.

## 3. Results

### 3.1. $^1\text{H}\text{-}^{29}\text{Si}$ Heteronuclear Correlation (HETCOR) MAS NMR Experiments

Figure 1 shows 2D  $^{29}\text{Si}\{^1\text{H}\}$  HETCOR MAS NMR spectra which were obtained for the  $\text{T}^{\text{H}}\text{D}^{\text{H}}1$  gel for two different  $t_c$  values. In the  $^1\text{H}$  dimension, two signals are present due to  $\text{Si-CH}_3$  ( $\delta = 0.2$  ppm) and  $\text{Si-H}$  ( $\delta = 4.6$  ppm) species, and in the  $^{29}\text{Si}$  dimension, the two peaks are characteristic of  $\text{D}^{\text{H}}$  ( $\delta = -35$  ppm) and  $\text{T}^{\text{H}}$  units ( $\delta = -85$  ppm). At short  $t_c$  ( $\sim 50$   $\mu\text{s}$ ), correlations are observed only between the two types of  $^{29}\text{Si}$  units and the  $\text{Si-H}$  proton species, indicating that the polarization transfer to  $^{29}\text{Si}$  nuclei occurs only from the directly bonded  $^1\text{H}$  nuclei. For longer  $t_c$  values (e.g.  $\sim 3$  ms), correlations are observed not only between the  $\text{Si-CH}_3$  groups and the  $\text{D}^{\text{H}}$  units, but also between these methyl protons and the  $\text{T}^{\text{H}}$  moieties. Analysis of the intensity variations of these correlation peaks with  $t_c$  (Fig. 2) allow the extraction of associated cross-relaxation  $T_{1\rho}$  times, which are characteristic of the respective  $^{29}\text{Si}\text{-}^1\text{H}$  dipolar coupling strengths. As expected, the values corresponding to dipolar interactions between the  $\text{Si-H}$  protons and the two  $^{29}\text{Si}$  sites are similar (ca. 100  $\mu\text{s}$ ). Interestingly, the cross-relaxation times associated with the dipolar interactions between the  $\text{Si-CH}_3$  protons and the two types of Si units are also similar (ca. 1.5 ms); this suggests a close spatial proximity between the  $\text{D}^{\text{H}}$  and  $\text{T}^{\text{H}}$  units.

### 3.2. 2D $^1\text{H}$ Homonuclear Correlation MAS NMR Experiments

Another way to probe the proximity of the two  $^{29}\text{Si}$  sites is to record a 2D  $^1\text{H}$  homonuclear correlation MAS NMR spectrum, to see whether  $^1\text{H}$  magnetization can

## Newly Applied Two-Dimensional Solid-State NMR Correlation Techniques 115

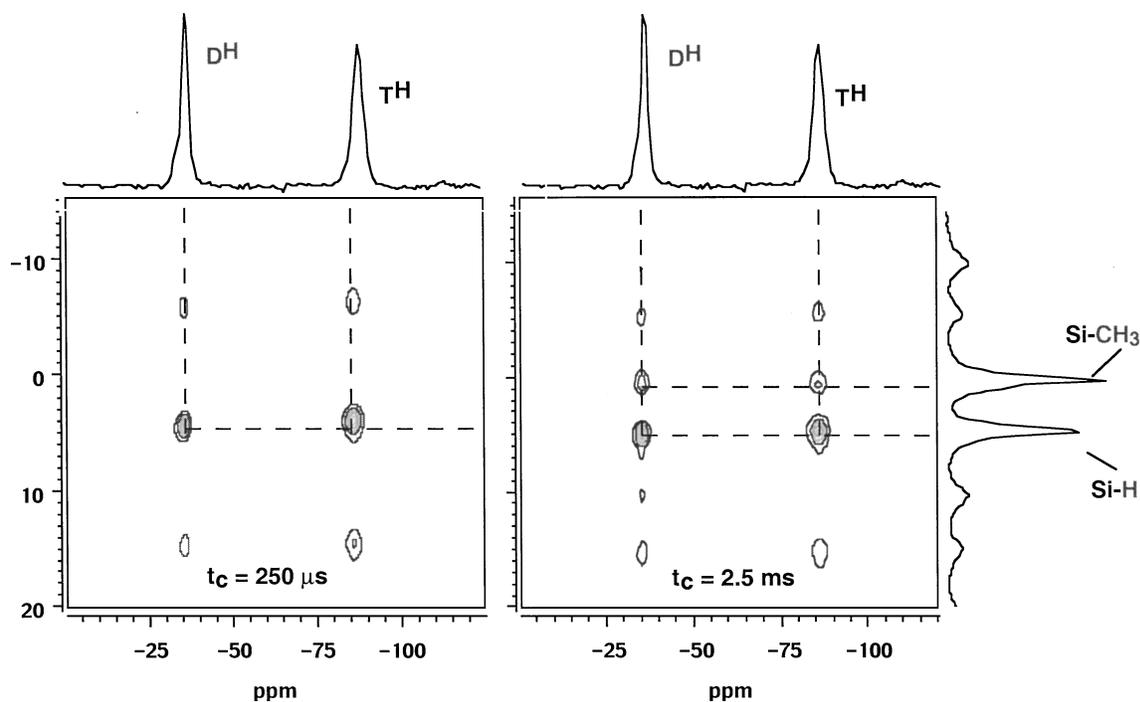


Figure 1. 2D  $^{29}\text{Si}\{^1\text{H}\}$  heteronuclear correlation MAS NMR spectra (contour plot) of  $\text{T}^{\text{H}}\text{D}^{\text{H}}\text{I}$  gel recorded for two contact times:  $300\ \mu\text{s}$  and 3 ms.

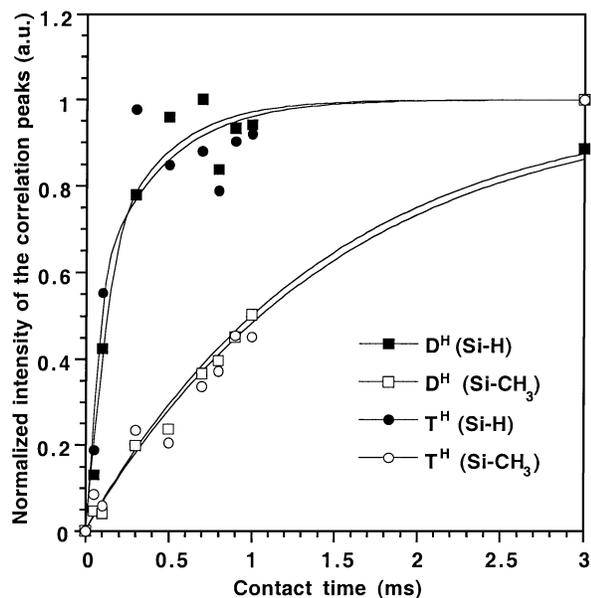


Figure 2. Variation, with contact time, of the intensity of the correlation peaks observed in the 2D  $^{29}\text{Si}\{^1\text{H}\}$  HETCOR experiments.

be transferred between different proton species [7, 8]. This kind of experiment requires high resolution  $^1\text{H}$  NMR spectra in order to distinguish the various proton sources. However solid-state  $^1\text{H}$  NMR spectra are

known to usually have relative poor resolution when using simple experimental conditions, due to strong homogeneous broadening from homonuclear dipolar interactions that are only partially averaged by MAS [9]. Multiple-pulse sequences combined with MAS have thus been developed to obtain better resolved spectra [10]. Using the combination of both high magnetic fields (14.1 to 18.8 T) and fast MAS spinning rates (up to 35 kHz), it is possible similarly to obtain large improvements in spectral resolution. For example, comparison of Fig. 3(a) and (b) illustrates the effect of magnetic field strength on the resolution of a  $^1\text{H}$  MAS-NMR spectrum of the  $\text{T}^{\text{H}}\text{D}^{\text{H}}\text{I}$  gel. At 14.10 T, two distinct signals are visible at 4.4 ppm and 4.8 ppm due to  $\text{SiH}$  groups in  $\text{T}^{\text{H}}$  and  $\text{D}^{\text{H}}$  units respectively with corresponding Full-Width-at-Half-Maximum (FWHM) of 220 and 185 Hz. A faster spinning rate of 30 kHz (Fig. 3(c)) produces still better resolution with respective FWHMs of 175 and 120 Hz. At 14.10 T and 30 kHz, 2D  $^1\text{H}$  homonuclear correlation spectra were recorded for different mixing times (Fig. 4), during which magnetization transfer may occur between the various proton species. Cross-peaks are not visible for short mixing times ( $t_m = 1$  ms), indicating that for this time scale, the  $\text{SiH}$  and  $\text{CH}_3$  groups can be considered to be isolated. The residual dipolar couplings, if any, between

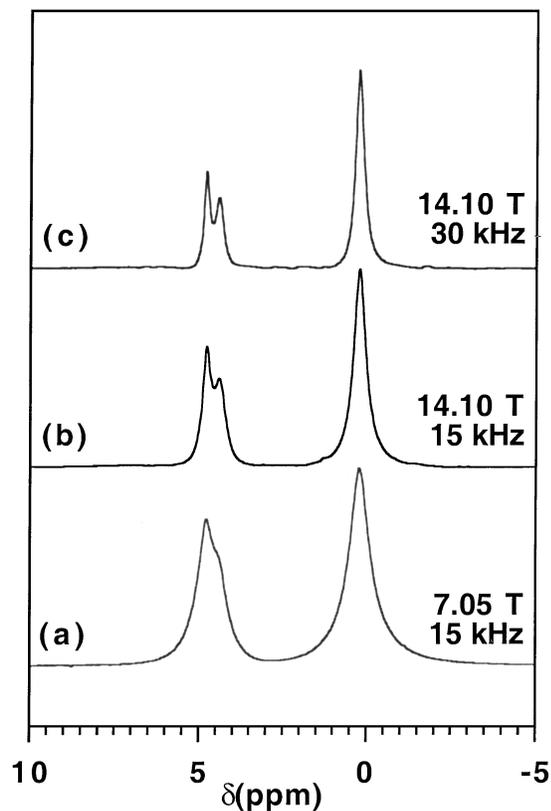


Figure 3.  $^1\text{H}$  MAS-NMR spectra of a gel prepared from co-hydrolysis of MDES and TREOS in a 1/1 ratio.

these species may lead to  $^1\text{H}$  magnetization exchange at longer mixing times. Indeed, cross peaks between the two types of  $\text{SiH}$  groups start to appear at  $t_m = 5$  ms while cross-peaks between each  $\text{SiH}$  type and the  $\text{CH}_3$  species are only present for  $t_m \geq 100$  ms (Fig. 4). Interestingly,  $^1\text{H}$  magnetization transfer is more efficient between  $\text{SiH}$  groups belonging to the two different types of Si units, rather than between the  $\text{SiH}$  and  $\text{CH}_3$  groups which belong to the same Si unit ( $\text{D}^{\text{H}}$ ). The presence of cross-peaks between the two  $\text{SiH}$  groups at short mixing times strongly suggests the existence of mixed domains in which the two Si units are in close contact.

#### 4. Conclusions

The solid-state 2D  $^{29}\text{Si}\{^1\text{H}\}$  heteronuclear correlation NMR experiments as well as the 2D  $^1\text{H}$  homonuclear correlation experiments can provide new insights on the structural proximity of different Si species in sol-gel derived siloxane-based materials. The information contents of such measurements are improved under conditions of high magnetic fields and fast MAS spinning rates. For a gel prepared from co-hydrolysis of methyldiethoxysilane and triethoxysilane, the 2D  $^{29}\text{Si}\{^1\text{H}\}$  heteronuclear correlation experiments recorded with variable contact time and the 2D

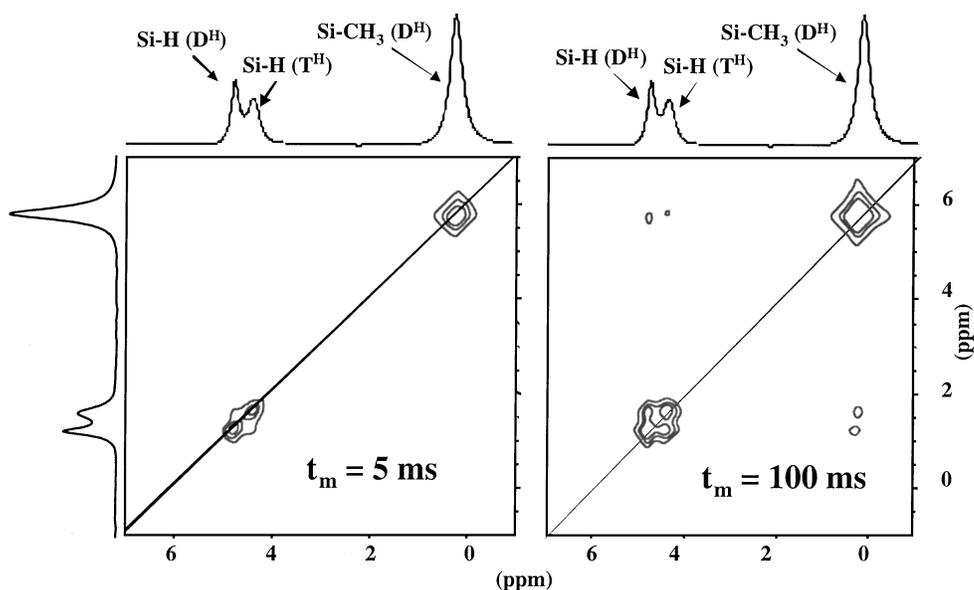


Figure 4. 2D  $^1\text{H}$  homonuclear correlation MAS NMR spectra of  $\text{T}^{\text{H}}\text{D}^{\text{H}}1$  gel recorded with mixing times of 5 and 500 ms.

$^1\text{H}$  homonuclear correlation experiments recorded with different mixing times have shown that the two types of silane units ( $\text{CH}_3\text{HSiO}$  and  $\text{HSiO}_{1.5}$ ) are in close dipolar contact, indicating chemically homogeneous network.

### Acknowledgments

This research is supported by the European Community TMR program ("Oxycarbide glasses" network). FB and BFC would like to acknowledge the CNRS and the U.S. National Science division of International Programs (Grant # INT-9726744) for a collaborative exchange program. FB and DM are grateful to Prof. G. Bodenhausen (Ecole Normale Supérieure, Paris) who made possible the  $^1\text{H}$  experiments on the 600 MHz spectrometer.

### References

1. D. Avnir, L.C. Klein, D. Levy, U. Schubert, and A.B. Wojcik in *The Chemistry of Organosilicon Compounds*, Vol. 2, edited by Y. Apeloig and Z. Rappoport (John Wiley & Sons Ltd, Chichester, 1998), Ch. 48.
2. V. Gualandris, F. Babonneau, M.T. Janicke, and B.F. Chmelka, *J. Sol-Gel Sci. & Techn.* **12**, 75 (1998).
3. A. Pines, M.G. Gibby, and J.S. Waugh, *J. Chem. Phys.* **59**, 569 (1973).
4. A.J. Vega, *J. Am. Chem. Soc.* **110**, 1049 (1988).
5. C.A. Fyfe, Y. Zhang, and P. Aroca, *J. Am. Chem. Soc.* **114**, 3252 (1992).
6. M.P.J. Peeters, W.J.J. Wakelkamp, and A.P.M. Kentgens, *J. Non-Cryst. Solids* **189**, 77 (1995).
7. P. Caravatti, P. Neuenschwander, and R.E. Ernst, *Macrom.* **18**, 119 (1985).
8. D.E. Demco, S. Haffner, C. Fülber, R. Graf, and H.W. Spiess, *J. Chem. Phys.* **105**, 11285 (1996).
9. K. Schmidt-Rohr and H.W. Spiess, *Multi-Dimensional Solid-State NMR and Polymers* (Academic Press, New York, 1994).
10. R.E. Taylor, R.G. Pembleton, L.M. Ryan, and B.C. Gerstein, *J. Chem. Phys.* **71**, 4541 (1979).