

Mesostructured Silica/Block Copolymer Composites as Hosts for Optically Limiting Tetraphenylporphyrin Dye Molecules

Nicholas A. Melosh,^{†,‡} Christian A. Steinbeck,[†] Brian J. Scott,[§] Ryan C. Hayward,[†] Patrick Davidson,[⊥] Galen D. Stucky,[§] and Bradley F. Chmelka^{*,†}

Department of Chemical Engineering, University of California, Santa Barbara, California 93106, Department of Chemistry and Biochemistry, University of California, Santa Barbara, California 93106, and Laboratoire de Physique des Solides, UMR CNRS 8502, Bat. 510, Université Paris-Sud, 91405 Orsay Cedex, France

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Transparent silica-block copolymer composites have been used as host matrices for optically limiting dye molecules to increase dye solubility and photophysical stability. For a given concentration, tetraphenylporphyrin (TPP)-doped mesostructured EO₁₀₆PO₇₀EO₁₀₆–silica composites exhibited improved optical limiting properties compared to wholly inorganic TPP-doped silica hosts. Increased TPP solubility within the PPO–PEO block copolymer allows higher concentrations of TPP to be incorporated without dye aggregation, enhancing optical absorption of incident laser light. In addition, the silica framework provides increased damage resistance to a series of intense laser pulses compared to wholly organic host matrices.

Introduction

Optical limiting materials and devices are of interest for applications in laser safety, sensor and vision protection, and optical switching.¹ These rely on the optical absorption properties of species that allow light at low intensities to pass essentially unobstructed, while higher intensities are attenuated much more strongly. Although a number of organic dye molecules show acceptable optical limiting properties in solution,^{2–10} solid-state systems tend to be more suitable for technological applications. It is therefore desirable to disperse the dye species in a transparent host material.

The selection of a suitable host matrix generally involves tradeoffs between absorptivity (dye concentration, solubility) and robustness (mechanical, laser damage resistance). Absorptivity is maximized by a high and macroscopically uniform dye concentration. High dye concentrations, however, risk exceeding dye solubility limits in a given host matrix, particularly in inorganic sol–gel glasses. Previous studies^{1,11–16} have shown that organic dye species occluded in inorganic silica glasses retained their optical limiting behavior and exhibited good photophysical stability. However, the extent of optical limiting was restricted by low dye solubilities in the relatively hydrophilic sol–gel-derived silica hosts. Alternatively, purely organic hosts, such as poly(methyl methacrylate) (PMMA), provide good solubilities for hydrophobic dye molecules but tend to be physically damaged at high laser intensities, decreasing their utility for optical limiting applications.¹⁷

One means of compromise between the superior stabilities of inorganic hosts and the higher dye solubilities presented by polymers is the use of organically modified silica (ORMOSIL)

networks. Results have shown that higher dye concentrations can be achieved in ORMOSILs than in silica glasses, yielding improved optical limiting properties, while maintaining some of the properties of wholly inorganic hosts.^{18–20} ORMOSILs, however, are inherently disordered blends, in which the organic and inorganic moieties are intimately mixed at a molecular level. The resultant materials properties are thus difficult to control independently. For example, increasing the dye solubility requires increasing the fraction of covalently bonded organic moieties in the ORMOSIL matrix, which can have adverse effects on the mechanical properties of the material.

An alternative approach is to use self-assembled mesostructured inorganic–organic composites as host materials for organic dyes. For example, mesostructured silica-block copolymer composites provide substantial versatility for combining desirable properties of the dissimilar inorganic and organic components.^{21–26} At sufficient concentrations, amphiphilic block copolymers locally separate into distinct hydrophilic and hydrophobic regions with uniform dimensions and periodicities in the range of 5–50 nm, according to the composition, structure, and lengths of the copolymer blocks. Selective incorporation and polymerization of soluble inorganic precursor species within the hydrophilic regions of the self-assembled copolymer blocks yield structures that combine the heightened thermal and mechanical stabilities of the inorganic framework with the high dye solubilities of the copolymer components. Unlike non-mesostructured organic/inorganic materials, where the domain sizes of organic and inorganic species can vary from angstroms to microns,²⁷ the structures of mesoscopically ordered block copolymer/silica composite solids are typically uniform and adjustable. Such self-assembled systems allow the mesoscale partitioning of the organic and inorganic components into regions that tend to preserve their distinct mechanical or solubility properties. For example, the surfactant properties of the block copolymer species can lead to reduced dye aggregation, which has been shown to limit the self-quenching of the laser dye rhodamine-6G in mesostructured silica-block copoly-

* To whom correspondence should be addressed.

[†] Department of Chemical Engineering, University of California, Santa Barbara.

[‡] Present address: Department of Materials Science and Engineering, Stanford University, Stanford, California 94305.

[§] Department of Chemistry and Biochemistry, University of California, Santa Barbara.

[⊥] UMR CNRS.

mer composites.²³ In addition, such materials can be prepared with high degrees of macroscopic alignment,^{25,28–32} which can be exploited to produce anisotropic optical properties for suitably large dye guest species. Furthermore, mesostructured organic–inorganic composite materials are processable into macroscopic fibers,³³ films,^{29,32,34} and monoliths,^{35–37} which can be integrated into a range of devices for optical applications.

Here, the properties and suitability of transparent mesostructured silica-block copolymer composites as host matrices for the incorporation of optically limiting tetraphenylporphyrin (TPP) guest molecules are examined. Porphyrins in general are one of the most intensely studied classes of organic dyes, because of their importance and abundance in many natural processes.³⁸ The large delocalized conjugate π -electron systems of macrocyclic porphyrins often exhibit significant nonlinear optical responses, which impart good optical limiting properties. Optical limiting in porphyrins is typically the result of reverse saturable absorption,¹⁰ which may occur if the excited state absorption cross-section of the dye species is higher than that of its ground state. For such systems, at low light intensities, absorption occurs almost exclusively from the weakly absorbing ground state, and light is transmitted with little loss. At higher light intensities, the population of the excited state increases and, because of its higher absorption cross-section, the light transmittance decreases significantly. The reverse saturable absorption properties of tetraphenylporphyrins and their derivatives in solution and also incorporated into wholly inorganic networks (e.g., aluminosilica sol–gel and borate glasses) have been studied previously.^{5,14,39–41} Organic/polymeric hosts doped with porphyrins have also been investigated^{42–44} but without emphasis on photostability, which is generally poor under intense irradiation.^{17,45} The mesostructurally ordered block copolymer/silica composites considered here combine the beneficial physical robustness of inorganic materials with the high solubility of organic dyes such as TPP, leading to an improved combination of optical and stability properties.

Experimental Section

Transparent block-copolymer/silica composites were synthesized using acidic silica sol–gel solutions containing nonionic poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (EO₁₀₆PO₇₀EO₁₀₆, Pluronic F127, BASF, Mount Olive, NJ) amphiphilic triblock copolymers in various concentrations. In a typical synthesis, 4.5 mL of tetraethoxysilane, (TEOS, Aldrich Chemicals) was hydrolyzed with 2.1 mL of HCl (pH = 1.4) and stirred until homogeneous. Subsequently, between 0 and 1.45 g EO₁₀₆PO₇₀EO₁₀₆ (corresponding to 0–55 wt % relative to SiO₂ in the final product) was added, followed by a quantity of tetraphenylporphyrin (TPP) in chloroform to obtain the desired concentration of TPP in the final composite ($\sim 8 \times 10^{-4}$ M). After mixing with the highly acidic silica/block copolymer solution, the initially red TPP became dark green, indicating protonation to TPPH₂²⁺.⁴⁶ The combined solutions were then transferred to Petri dish molds (4 cm in diameter) and loosely covered for 3 days. At the end of this period, during which solvent evaporation and silica cross-linking occur, the products had shrunk by 10–50% in diameter, resulting in ~ 1 -mm thick, ~ 2.5 -cm diameter transparent green disks.

The degree of mesostructural ordering was evaluated by conducting two-dimensional (2D) X-ray diffraction (XRD) experiments at the D43 experimental station of the LURE synchrotron facility (Orsay, France),⁴⁷ as previously described.⁴⁸ A single bent Ge monochromator was used to select a

wavelength of 1.448 Å, and the beam was collimated to a diameter of 0.5 mm. Diffraction patterns were collected on phosphor image plates and scanned with a pixel size of 200 $\mu\text{m} \times 200 \mu\text{m}$, with an exposure time of 1–5 min. The sample-to-detector distance was calibrated using silver behenate ($d_{001} = 5.838$ nm). Monolith samples were positioned with the X-ray beam perpendicular or parallel to the plane of the disks to probe for orientational ordering of the mesophase structures.

Measurements of optical limiting properties were performed using the second harmonic of a Nd:YAG laser at 532 nm with 10 ns pulse widths and intensities of up to 4 mJ/pulse at a frequency of 2 or 10 pulses/s. The beam was typically focused to a spot approximately 1 mm in diameter, and the transmitted intensity was measured with a Melectron power meter relative to the incident light intensity, $I_{\text{trans}}/I_{\text{incid}}$. Samples were prepared to contain bulk dye concentrations of 8×10^{-4} M TPP, based on bulk densities of 2.6 g/cm³ for fully condensed silica and 1.0 g/cm³ for the F127 triblock copolymer species. To compare the optical limiting and damage resistance properties of different samples, the dye concentration of each region probed was normalized according to its absorbance at 532 nm, as measured by UV–vis spectroscopy over the wavelength range from 280 to 1100 nm.

Results and Discussion

Mesoscopic Ordering of the Host Matrix. Prior to performing optical limiting measurements, the extent of mesoscopic ordering in each of the composite materials was determined by using small-angle X-ray diffraction measurements. It has been previously demonstrated^{30,37} that the degree of mesoscopic ordering in transparent silica/PEO–PPO–PEO monoliths depends on the concentration of the block copolymer. X-ray diffraction measurements of such transparent monoliths without and with low (8×10^{-4} M) concentrations of organic dye species show increased extents of mesoscopic organization at higher concentrations of the structure-directing block copolymer species. Figure 1 shows two-dimensional (2D) XRD patterns collected for a series of silica/EO₁₀₆PO₇₀EO₁₀₆ composite monoliths containing 8×10^{-4} M tetraphenylporphyrin dye species and different concentrations of the F127 triblock copolymer species. Corresponding integrated azimuthal intensity plots accompany the 2D XRD patterns, which were acquired with the X-ray beam perpendicular to the plane of each disk monolith. As shown in Figure 1a, the composite containing 35 wt % F127 yields only a single weak ring of scattering intensity at a d -spacing ($2\pi/q$) of approximately 10 nm ($q \sim 0.62$ nm⁻¹). This is indicative of a structure that is partially locally phase-separated, but with little long-range mesoscopic ordering. As expected, increasing the PEO–PPO–PEO triblock copolymer content to 45 wt % and then to 55 wt % F127 results in increased diffraction intensity and narrower diffraction peaks, as well as the appearance of higher order reflections, as seen in parts b and c of Figure 1, respectively. The d -spacings increase with block copolymer content to 11.2 nm ($q \sim 0.56$ nm⁻¹) at 45 wt % and 13.1 nm ($q \sim 0.48$ nm⁻¹) at 55 wt % F127. The 2D XRD pattern obtained from the 45 wt % F127 monolith consists predominantly of a diffuse halo, along with a few discrete spots. This indicates that, although the monolith has appreciable mesoscopic order, the organization does not persist over large domains. By comparison, the 2D XRD pattern of the 55 wt % F127 monolith consists of a number of discrete spots at small scattering angles, establishing that the regions probed by the X-ray beam (~ 1 mm³) contain large well-ordered mesostructured domains. The presence of a higher order peak at $\sqrt{2}$ times

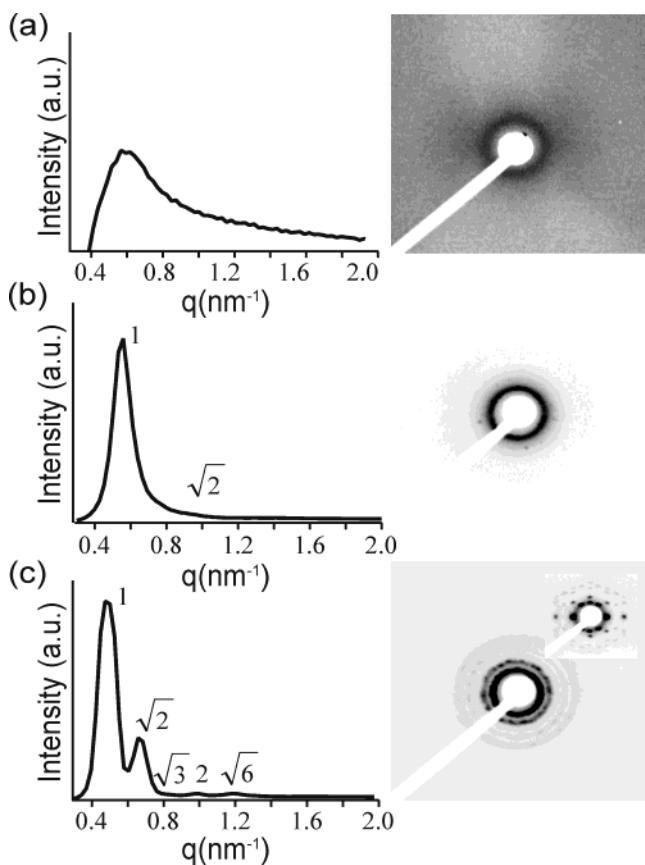


Figure 1. Small-angle X-ray diffraction patterns obtained from transparent silica/EO₁₀₆PO₇₀EO₁₀₆(F127)/ 8×10^{-4} M tetraphenylporphyrin (TPP) composite monoliths containing different weight percents of the amphiphilic triblock copolymer: (a) 35, (b) 45, and (c) 55 wt % F127. Plots of intensity versus scattering vector modulus q represent azimuthal integrals of the 2D scattering patterns obtained with the X-ray beam oriented perpendicular to the planes of the disk monoliths. The small inset in part c is the pattern obtained for the 55 wt % F127 sample with the X-ray beam oriented parallel to the disk plane. The extent of mesoscopic organization increases with increasing block copolymer concentration over the range of compositions examined.

the reciprocal lattice spacing of the primary reflection suggests that the ordered regions of the 55 wt % F127 sample exhibit a cubic mesostructure. Furthermore, scattering patterns collected with the X-ray beam parallel to the monolith disk plane show that the mesostructure of the monolith containing 55 wt % F127 is orientationally ordered. The inset pattern shown in Figure 1c reveals a large number of discrete spots that are indexable according to a cubic $Im\bar{3}m$ symmetry with the [110] direction oriented perpendicular to the disk plane.

Dye Distribution. The distributions of the TPP dye species within the bulk silica/PEO-PPO-PEO composite materials depend on their block copolymer contents. The optical micrographs in Figure 2a,b, for example, show clearly that the dye species are not homogeneously distributed within bulk composites containing relatively low concentrations of the triblock copolymer species. Macroscopic aggregates of the TPP dye with characteristic sizes on the order of $50 \mu\text{m}$ are observed as dark spots in the micrographs for the 0 and 35 wt % F127 triblock copolymer/silica materials, which have little or no mesoscopic order. Such macrophase separation into TPP aggregates that are on the order of the wavelength of light leads to increased scattering of incident light, reduced transparency, inhomogeneous optical properties, and reduced overall performance. Under the conditions used to prepare the TPP/F127/silica composites discussed here, the maximum concentration of TPP

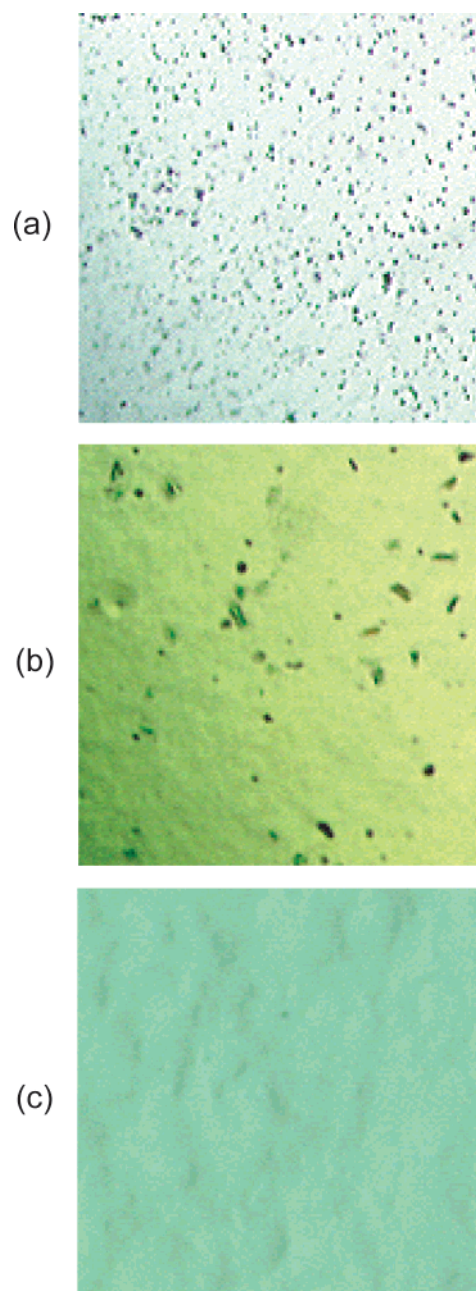


Figure 2. Optical micrographs ($5\times$ magnification) of silica/EO₁₀₆PO₇₀EO₁₀₆ composite monoliths containing 8×10^{-4} M tetraphenylporphyrin (TPP) dye species and (a) 0, (b) 35, and (c) 55 wt % of the F127 triblock copolymer species. The micrographs reveal macroscopically phase-separated $50 \mu\text{m}$ aggregates of TPP in the composites containing 0 and 35 wt % F127 and a more homogenous dye distribution in the sample containing 55 wt % F127. Each micrograph shows a representative area of 9mm^2 .

that could be homogeneously incorporated into sol-gel-derived silica glass containing 0 wt % F127 before macroscopic TPP aggregates formed was approximately 2×10^{-4} M. By comparison, the optical micrograph in Figure 2c of the 55 wt % F127 triblock copolymer/silica/TPP composite shows no detectable opacity or evidence of dye aggregation at 8×10^{-4} M.

UV-vis absorption spectra, shown in Figure 3, indicate that the TPPH₂²⁺ molecules are preferentially associated with the amphiphilic triblock copolymer species in the F127/silica composites. The UV-vis spectrum of TPP incorporated into sol-gel-derived silica glass (0 wt % F127) exhibits an absorption maximum at wavelength $\lambda_{\text{max}} = 654 \text{nm}$, corresponding to

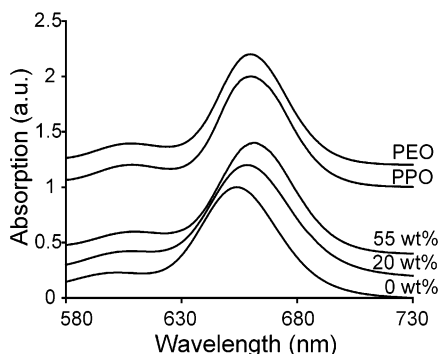


Figure 3. Stacked UV-vis absorption spectra of silica/EO₁₀₆PO₇₀-EO₁₀₆ (0, 20, and 55 wt % F127) composite monoliths containing 8×10^{-4} M TPP and of homopolymers PEO and PPO containing 8×10^{-4} M TPP. The spectra are offset vertically for clarity.

the absorption of diprotonated TPP dimers in water-ethanol solutions.⁴⁹ By comparison, TPP incorporated into the separate PEO and PPO homopolymers and all of the TPP/F127/silica composites exhibit absorption maxima at $\lambda_{\text{max}} = 660$ nm; representative spectra for the 20 wt % and 50 wt % F127 monoliths containing 8×10^{-4} M TPP are shown. This indicates that the local environments of the TPP molecules in the different composite samples are equivalent within the sensitivity of the measurements, though different from TPP in silica glass. The absorption spectra of TPP in hydrophilic and hydrophobic environments are expected to be different, due to the differing extents to which the excited state is stabilized. Such stabilization can result in a red shift of the maximum absorbance wavelength or a change in the sideband intensities, according to local interactions between the solvent and the dye molecules in their excited states.⁵⁰ Although these data support preferential association of the TPP species with the triblock-copolymer components, as opposed to the inorganic framework, differences in local TPP environments due to solvation in PPO, versus PEO-rich regions, could not be distinguished. Efforts are underway in our laboratory to examine in greater detail the molecular environments and dynamics of the porphyrin dye species within self-assembled block copolymers and block copolymer-silica composite monoliths.

Optical Limiting Properties. Optical limiting measurements establish that highly mesostructurally ordered silica/EO₁₀₆PO₇₀-EO₁₀₆ composites yield enhanced light absorption responses for a given TPP concentration, compared to less ordered composites or wholly inorganic silica glasses. Figure 4 shows the optical limiting properties measured for TPP-doped mesostructured block copolymer-silica composites and sol-gel-derived silica glasses with similar bulk dye concentrations. All of the materials exhibit optical limiting behaviors for incident light intensities greater than approximately 30 mJ/cm², as evident from the logarithmic plots of transmittance versus incident light intensity shown in Figure 4a. Above this threshold of incident light intensity, the transmittances drop sharply, with the corresponding differential decreases correlated with the amount of F127 in the composites and the corresponding extents of TPP dispersion. Greater dispersion of the TPP dye species in the 45 and 55 wt % F127-silica composites leads to increased absorption of incident laser light and, thus, improved optical limiting properties for these mesostructured materials.

Up to incident light intensities of 200 mJ/cm², incident light is increasingly attenuated, whereas above this intensity, the light transmittances allowed by the materials level off. As shown in Figure 4b, the apparent limiting values of transmitted light do not scale linearly with block copolymer content, but rather

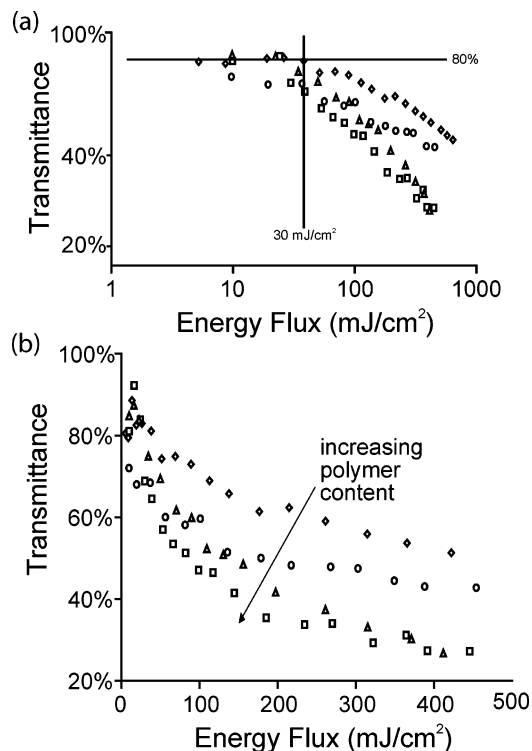


Figure 4. Optical transmittances plotted as functions of incident light intensity for 1-mm thick TPP-doped (8×10^{-4} M) silica/EO₁₀₆PO₇₀-EO₁₀₆ composites containing various concentrations of the triblock copolymer species: 0 (\diamond), 29 (\circ), 45 (\triangle), and 55 wt % F127 (\square). The data are presented both on (a) log-log and (b) linear scales to illustrate threshold and limiting transmittance behaviors, respectively. Optical limiting is clearly evident above a threshold intensity of incident light of approximately 30 mJ/cm². The two samples with higher concentrations of the structure-directing block copolymer (45 and 55 wt % F127) display significantly lower limiting optical transmittances compared to the samples without mesostructural order (0 and 29 wt % F127). The measured light transmittances were corrected for small differences in their respective concentrations of TPP arising during the synthesis process, as described in the text.

depend on the degree of microphase-separation of the composite material. The 45 and 55 wt % EO₁₀₆PO₇₀EO₁₀₆/silica/TPP composites absorb approximately 75% of the incident laser light at high intensities (~ 400 mJ/cm²), whereas the composites containing 0 and 29 wt % F127 block copolymer absorb only 50% or less at the same incident light intensities. As the bulk TPP loadings in the different composites are identical, the differences in the limiting transmission values are most likely due to differences in the local environments and dispersions of the TPP species, particularly with respect to dye aggregation. The presence of macroscopic dye aggregates in the TPP/F127/silica composites is expected to have a deleterious effect on the optical limiting properties of the materials for at least two reasons. First, dye aggregation within composites containing lower amounts (<40 wt %) of F127 can lead to excited states with shorter lifetimes, as exciton-exciton annihilation becomes a possible relaxation pathway in aggregated structures.⁶ This explanation has also been invoked, for example, to account for the absence of optical limiting behavior in solid samples of C₆₀ fullerenes.⁵¹ Second, the formation of large, on the order of 50- μ m, phase-segregated TPP aggregates leads to inhomogeneous distributions of dye molecules in the regions probed by the incident light beam, with localized areas of high dye concentration and large areas of relatively low concentration. Such a distribution leads to an overall reduction in optical absorption efficiency, because light transmittance is exponen-

tially dependent on concentration, $I_{\text{trans}}/I_{\text{incid}} = e^{-\epsilon bc}$, where $I_{\text{trans}}/I_{\text{incid}}$ is the ratio of the transmitted and the incident light intensities, b is the sample thickness, ϵ is the molar absorptivity, and c is the concentration of the absorbing species. The total transmittance is therefore not a simple average over all molecules, as areas with high concentration will absorb less incident light per molecule than areas of low concentration. Enhanced dispersion of the TPP dye species within the mesostructured 45 and 55 wt % EO₁₀₆PO₇₀EO₁₀₆/silica composites correlates strongly with the improved optical limiting properties of these materials.

Optical Stabilities. Having established the increased dispersion and enhanced optical absorption of TPP dye species within the mesoscopically ordered EO₁₀₆PO₇₀EO₁₀₆/silica composites (45 and 55 wt % F127), compared to samples exhibiting little or no mesoscopic ordering (0 and 35 wt % F127), the damage resistances of these materials to intense laser light were assessed. Representative optical micrographs are shown in Figure 5 of the 0, 35, and 55 wt % F127/silica composites after exposure to 3000 pulses of laser light, each with an incident energy of approximately 100 mJ/cm². Notably, evidence of macroscopic mechanical damage is clearly observed in regions of the 0 and 35 wt % EO₁₀₆PO₇₀EO₁₀₆/silica/TPP composites (Figure 5a,b) after exposure to repeated intense laser pulses. The macroscopic cracking is likely due to local heating induced by the laser pulses, which produce large temperature gradients and accompanying stresses within the cross-linked silica network. Residual solvent contents (such as adsorbed/occluded water, up to approximately 10 wt %^{52,53}) could also contribute to localized mechanical stresses as a result of rapid laser-induced solvent desorption/vaporization. After similar prolonged laser pulsing, no discernible macroscopic fracturing is observed in the 55 wt % F127 triblock copolymer-silica composite (Figure 5c). The lighter bleached area indicates partial photodecomposition of the TPP; however, the host matrix does not appear to be damaged. This is consistent with the greater mechanical elasticity of the materials expected at higher triblock copolymer contents, which appear thus to better accommodate thermally induced structural stresses.

Prolonged exposure to intense laser irradiation has a measurable, although minor, effect on the optical responses of the various composites. As shown in Figure 6, the optical stabilities of all of the samples were high, with none showing changes in transmittance of more than approximately 1% after 3000 laser pulses. For the laser intensities, pulse rates, and number of incident pulses used here, the mesostructured F127/silica/TPP composites show optical stabilities that are comparable to those of the wholly inorganic glass systems.⁵⁷ Nevertheless, samples with higher block copolymer contents display slightly more sensitivity to damage, consistent with the lower damage resistances of dyes incorporated into wholly organic host matrices,^{17,54–56} compared to inorganic glasses.^{11–17}

Conclusions

In summary, mesostructured PEO–PPO–PEO/silica composites are suitable host matrices for optical limiting tetraphenylporphyrin (TPP) dye species, combining many of the beneficial properties of sol–gel-derived silica glasses and wholly organic polymer host systems. Compared to the inclusion of TPP in amorphous silica glass, the presence of the mesostructure-directing PEO–PPO–PEO triblock copolymer species permits higher concentrations of dispersed TPP dye molecules to be incorporated into the composites. The amphiphilic triblock copolymer species promote better dispersion of the dye molecules within the organic regions of the mesostructured com-

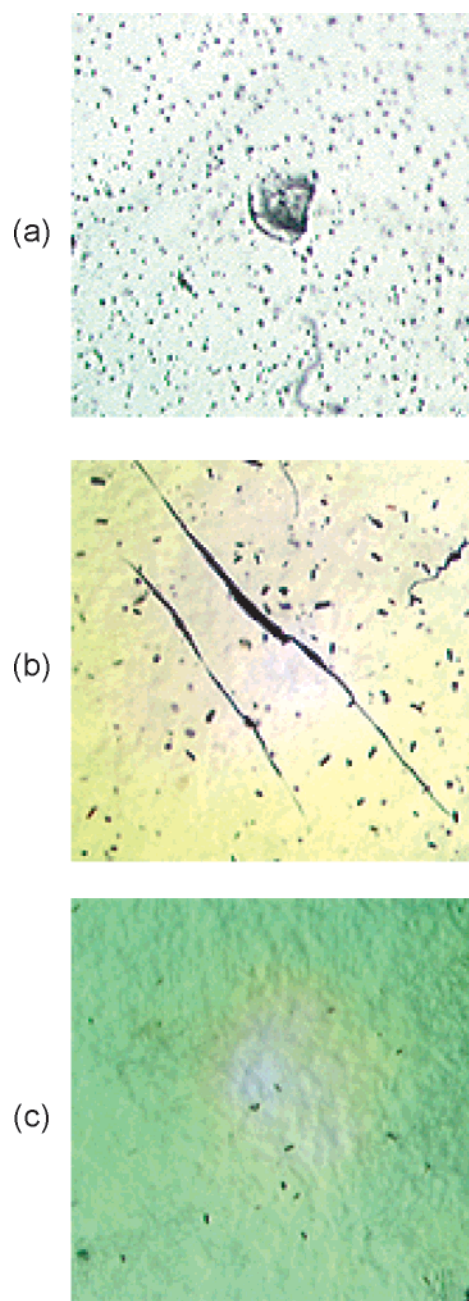


Figure 5. Optical micrographs (5× magnification) showing laser-damaged areas of different silica/EO₁₀₆PO₇₀EO₁₀₆ composites containing 8×10^{-4} M TPP and different triblock copolymer compositions: (a) 0, (b) 35, and (c) 55 wt % F127. Each micrograph depicts an area of 9 mm², following exposure to 3000 10-ns incident laser light pulses (532 nm, 97 mJ/cm²) at 10 Hz.

posite, leading to improved optical limiting properties. Furthermore, the optical damage resistance of the TPP dye species incorporated in the EO₁₀₆PO₇₀EO₁₀₆ block copolymer-silica composites remains significantly better than for wholly organic host matrices.

The mesostructured PEO–PPO–PEO/silica composites are in many aspects superior to strictly organic or inorganic host systems for optical limiting dyes and an interesting alternative to ORMOSILS. The 45 and 55 wt % F127/silica/TPP composites, for example, allow relatively high TPP concentrations to be incorporated without formation of undesirable dye aggregates, while maintaining good damage resistance properties. The sensitivity to photobleaching and optical property degradation is relatively low, and the mesostructured composite host matrices

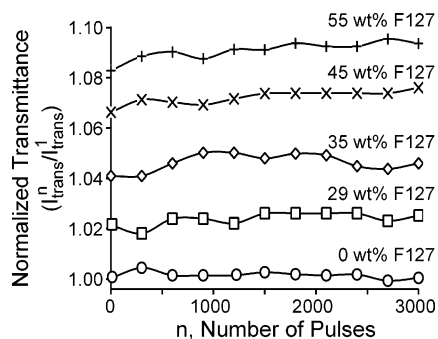


Figure 6. Optical transmittances plotted as functions of the number of incident laser pulses for TPP-doped (8×10^{-4} M) silica/EO₁₀₆PO₇₀-EO₁₀₆ composites containing different concentrations of the triblock copolymer species (same as in Figure 4): 0 (○), 29 (□), 35 (◇), 45 (×), and 55 wt % (+). Transmittances were measured at 532 nm with 10 ns laser pulses at 10 Hz, with an incident intensity of 97 mJ/cm². The plots are offset vertically for clarity.

maintain their integrities even under repeated exposure to intense (100 mJ/cm²) laser pulses. For many applications, optical limiting would not be required for thousands of intense pulses; rather a few laser bursts at high intensity might generally be anticipated. Consequently, the 45 or 55 wt % F127/silica/TPP composites appear to be suitable candidates for optical limiting applications. Such self-assembled PEO-PPO-PEO/silica composites demonstrate how tailoring and control of mesoscale compositions and structures can be used to design and synthesize materials with novel combinations of properties.

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