GLASSY POLYSTYRENE COMPOSITES HAVING ZEOLITE 13X OR VYCOR AS A DISPERSED INORGANIC PHASE

Shahin Maaref[a]; Harry L. Frisch[a]; Guru S. Rajan[b]; Zhengcai Pu[b]; James E. Mark[b]; Gregory Beaucage[c]
[a] Department of Chemistry, State University of New York at Albany, Albany, NY, U.S.A. [b] Department of Chemistry and the Polymer Research Center, The University of Cincinnati, Cincinnati, OH, U.S.A. [c] Department of Materials Science and Engineering, The University of Cincinnati, Cincinnati, OH, U.S.A.

PLEASE SCROLL DOWN FOR ARTICLE

GLASSY POLYSTYRENE COMPOSITES HAVING ZEOLITE 13X OR VYCOR AS A DISPERSED INORGANIC PHASE

Shahin Maaref and Harry L. Frisch

Department of Chemistry
State University of New York at Albany
Albany, NY, 12222

Guru S. Rajan, Zhengcai Pu, and James E. Mark*

Department of Chemistry
   and the Polymer Research Center
The University of Cincinnati
Cincinnati, OH, 45221-0172

Gregory Beaucage

Department of Materials Science and Engineering
The University of Cincinnati
Cincinnati, OH, 45221-0012

Key Words: Polystyrene, Hybrid Organic/Inorganic Composites, Zeolite 13X, Vycor, Glass Transition Temperatures, Mechanical Properties, Filler Dispersion

ABSTRACT

Hybrid organic/inorganic composites were prepared from polystyrene as the organic phase and a zeolite or Vycor glass as the inorganic phase. The resulting materials were characterized using differential scanning calorimetry, Instron testing, scanning electron microscopy, and small-angle X-ray scattering. Correlations

---

* Author to whom correspondence should be addressed.

1895

among these results were used to obtain insights into structure-property relationships for these types of materials.

INTRODUCTION

There has been an increased interest in the preparation and characterization of hybrid composites of organic phases (typically polymers) with inorganic phases (typically ceramics) [1-12]. In the oldest preparative technique, such materials were prepared as blends, in which the inorganic filler material was dispersed either in a melt, or by use of a suitable polymer solution with the solvent subsequently evaporated. More recently, nanocomposites have been prepared by newer, novel techniques, including *in-situ* precipitation of the inorganic phase into a polymer matrix, and "threading", e.g., growing (polymerizing) polymer chains through porous fillers to produce intimate contacts between the phases in the resulting composite [4, 9-11]. The threaded materials can be termed pseudo (or semi) interpenetrating polymer networks (PIPNs) in analogy to their well known fully organic analogs. In the blending, *in-situ*, and threading approaches, the dispersed phase can give particularly good reinforcement in the case of elastomeric polymers. Much less studied, is the case where the polymeric matrix is in the glassy state, since little reinforcement is generally observed under these conditions.

The present investigation was carried out to obtain some insight into the properties of such less-studied systems. Specifically, glassy polystyrene (PS) was chosen as the organic polymer continuous phase, and either Zeolite 13X or Vycor glass as the dispersed inorganic phase. Since the polymer was in the glassy state, the first property investigated was the glass transition temperature T_g. This was done using differential scanning calorimetry (DSC), and the focus was on how T_g was affected by the dispersed phase. Uniaxial elongation measurements were also carried out, to see whether there might be any changes in brittleness resulting from the presence of the dispersed phase. The main focus, however, was on the morphology of these materials, parts of the investigation were carried out using scanning electron microscopy (SEM) and small-angle X-ray scattering (SAXS).

EXPERIMENTAL

Materials

All materials were purchased from the Aldrich Chemical Co., except for the Vycor glass (which was obtained from the Corning Corporation). Styrene

monomer (reagent grade, 99%) was washed with 10% potassium hydroxide solution, followed by distilled water, dried over anhydrous sodium sulfate, and then twice distilled at 10 torr and 59°C. Zeolite 13X (crystalline Na_2O: Al_2O_3: 2.8 ± 0.2 SiO_2:X H_2O) had a pore size of 9-10 Å and mean particle size of 3-5 μm. It was dried for two days in a vacuum oven at 200°C prior to use. The Vycor glass (amorphous SiO_2: 0.25 B_2O_3: 0.06 Na_2O) had a pore distribution with peaks lying between 40 and 60 Å, with a mean particle size of 20-40 μm. This material was dried for 2 days in a vacuum oven at 600°C before use. Other materials were used as received.

These materials were employed as described below to prepare a reference sample of unfilled PS, samples of polymer-filler blends, and corresponding samples of some PIPNs.

Preparation of Composites

A reference sample of linear, unfilled PS was prepared by adding benzoyl peroxide initiator (1% by weight) to the distilled styrene monomer. Viscometric measurements in toluene at 30°C indicated that the resulting polymer had a viscosity-average molecular weight of $M_v = 4.2 \times 10^5$ [13].

Both the blend samples and the PIPN samples were prepared so as to contain either 5 or 10 wt% filler. The blend samples were prepared by adding chloroform solvent to the linear PS and then mixing into the resulting solution the chosen amount of either the zeolite or Vycor. The resulting slurries were then poured into aluminum molds (one with dimensions 15 cm × 7.5 cm × 2 mm, and the other with 15 cm × 7.5 cm × 0.5 mm). The composites were obtained by evaporating the solvent at 70°C and the remaining mixtures were further polymerized at 110°C after they were maintained for two days under 2000 psi in a Carver press.

The PIPNs were prepared by blending the fillers into styrene monomer and benzoyl peroxide initiator. The resulting mixtures were polymerized at 110°C after they were maintained for two days under 2000 psi in a Carver hydraulic press.

Differential Scanning Calorimetry

DSC measurements were carried out on the samples under nitrogen gas in a Du Pont 2910 apparatus. Multiple runs were obtained at a scanning rate of 20°C/min and were confirmed by subsequent measurements at a scanning rate of 40°C/min.

Instron Testing

Mechanical strength measurements were performed on thin film samples using an Instron Tester (Series IX Automated Materials Testing System V4.12b). Samples having an initial length of 30 mm were tested at a crosshead speed of 12.7 mm/minute. The data acquisition speed was 5 points/second and tests were performed at 25°C and 50% humidity.

Scanning Electron Microscopy

SEM micrographs were taken on a Digital Scanning Microscope (DSM 940, Zeiss, Germany). The samples had been coated with gold (100 Å) on a Balzers SCD 004 Sputter Coater. The electron images were recorded directly from the cathode ray tube onto Polaroid 55 film.

Small-Angle Scattering Measurements

SAXS measurements were conducted on a 10 m pinhole camera at Oak Ridge National Laboratory. Data were corrected to absolute intensities by measurements of sample thickness and through comparison with secondary standards [10].

RESULTS AND DISCUSSION

Glass Transition Temperatures

Values of T_g obtained from the calorimetric studies are presented in Table 1. The blends and PIPNs having the lower wt% are seen to have lower values of T_g relative to that of pure unfilled PS. It is not clear whether the surface of the fillers was completely wetted by PS. If not, this could introduce free cavities into the samples and increase the local free volume. For both types of composite, the depression of the T_g increases with higher weight percent of the filler. There is a similar increase in going from the zeolite to the Vycor which has increased pore size and particle size. Presumably, these changes are also due to increases in free-volume [14].

Mechanical Properties

The stress-strain isotherms for the reference PS and the composites are shown in Figure 1 (a, b). These curves provide values of Young's modulus, ten-

TABLE 1. Glass Transition Temperatures (°C)

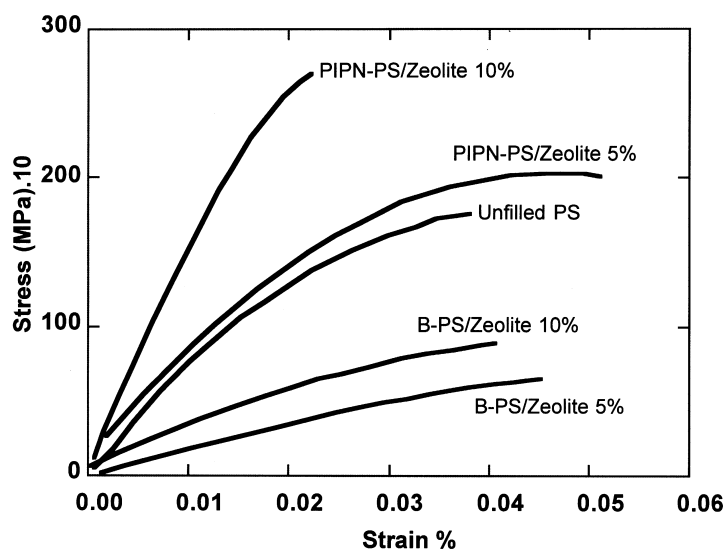| Composite	Pure	Blend	PIPN
Unfilled PS	97	--	--
PS/Zeolite 5%	--	94	96
PS/Zeolite 10%	--	81	80
PS/Vycor 5%	--	79	80
PS/Vycor 10%	--	76	77

Figure 1.   (a) Stress-strain isotherms for the PIPN (PIPN-PS/Zeolite) and blend (B-PS/Zeolite) samples of polystyrene filled with zeolite 13X;   (b) Stress-strain isotherms for the PIPN (PIPN-PS/Vycor) and blend (B-PS/Vycor) samples of polystyrene-filled Vycor glass. The compositions are specified by the wt% filler incorporated.

sile strengths, and maximum extensibilities of the zeolite 13X and Vycor filled samples. With regard to the zeolite 13X fillers, the blends showed no reinforcement effects, but the PIPNs at least showed significant increases in tensile strength with increasing weight percent filler. As frequently occurs, however, there were corresponding decreases in maximum extensibility. In the case of the Vycor filler, there was no reinforcement for either the blends or PIPNs. Apparently, the particle size of the Vycor was too large to show any reinforcing capabilities. This is consistent with the effects of fillers in non-elastomeric materials in general [15]. Presumably, improvements would be obtained at temperatures above the glass transition temperatures of these materials.

It is interesting to note that the PIPN samples gave larger values of the tensile strength relative to the corresponding blended samples. This could possibly be due to increased interfacial interactions in the PIPNs.

**Particle Sizes and Degrees of Dispersion**

Electron Micrographs

SEM results shown in Figure 2 (a-d) are consistent with the stated average particle size of the zeolite filler being 3-5 μm and that of the Vycor 20-40 μm. PS filled with the zeolite exhibited a uniform crystal size, unlike that of Vycor, as shown in Figure 2 (a, c). Larger aggregates in the zeolite may be due to the PS molecules sticking to its external and internal surfaces and binding them together. This is not seen in the Vycor samples, as shown in Figure 2 (b). Figure 2 (d) demonstrates that the zeolite particles are well distributed and well embedded throughout the entire sample.

Scattering Results

Figure 3 shows the SAXS results from three Vycor samples: powder, 10% PIPN and 50% PIPN. Previous studies of polymer/zeolite 13X composites have demonstrated penetration of the polymers into the zeolite pores [16]. The penetration into zeolites was demonstrated in the previous study by variation in the scattering pattern above 0.1 Å^{-1}, since the pores are smaller than $2\pi/0.1$ Å = 63 Å (Bragg's Law). For leached Vycor glass, the pores are larger than 63Å so features corresponding to the pore size appear below q = 0.1 Å^{-1}. The peak in the Vycor curves corresponds to the correlation peak for the phase-separated glass structure prior to leaching [17]. In previous studies by Schaefer [17], a power-law decay with a -3.3 slope was observed in the SAXS from leached Vycor glass
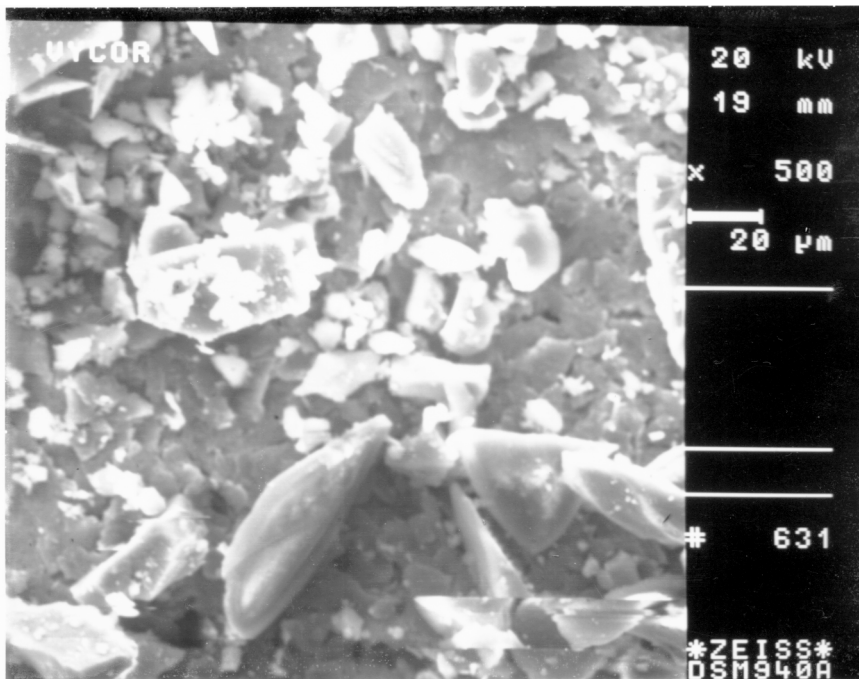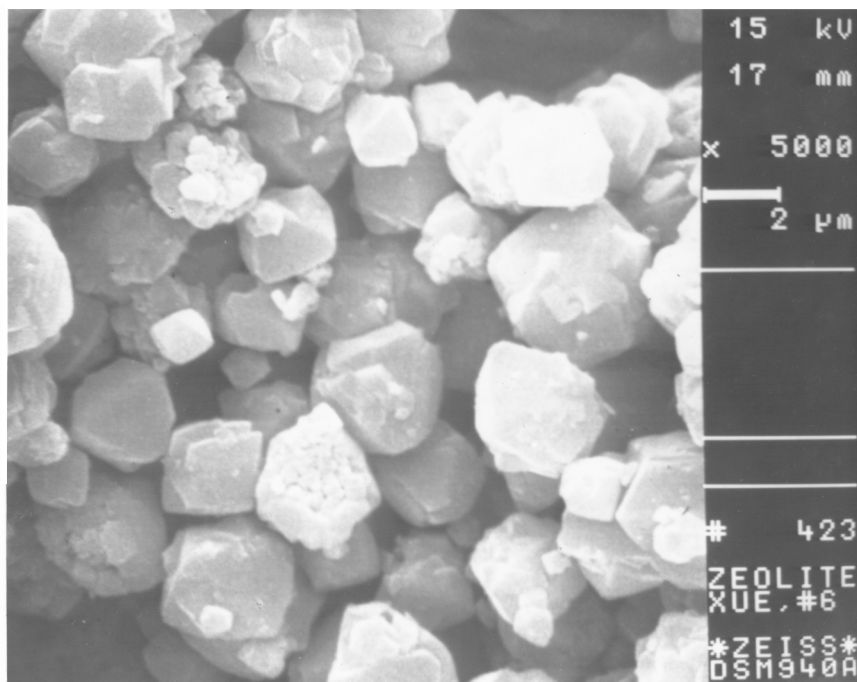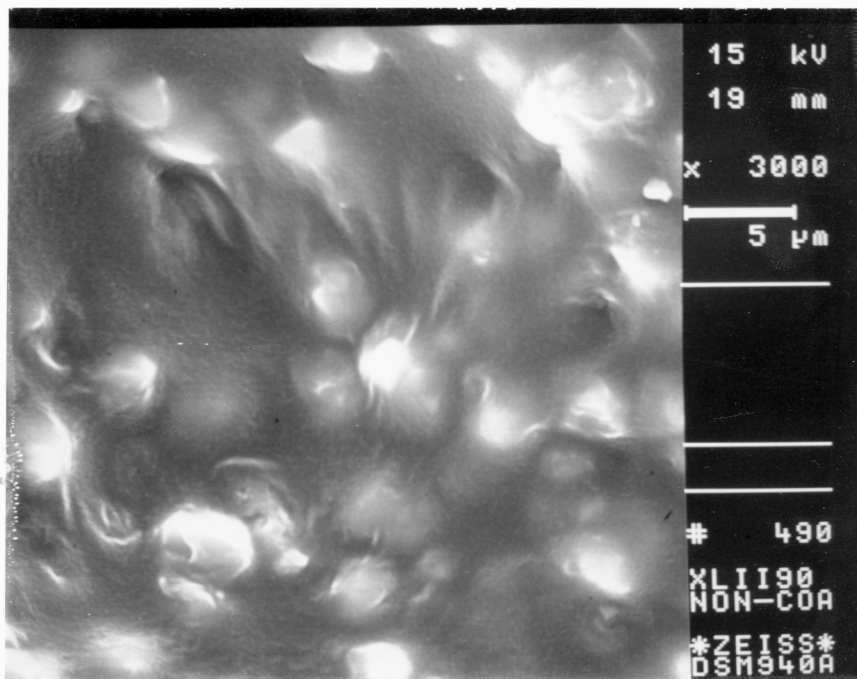
(a) pure Vycor
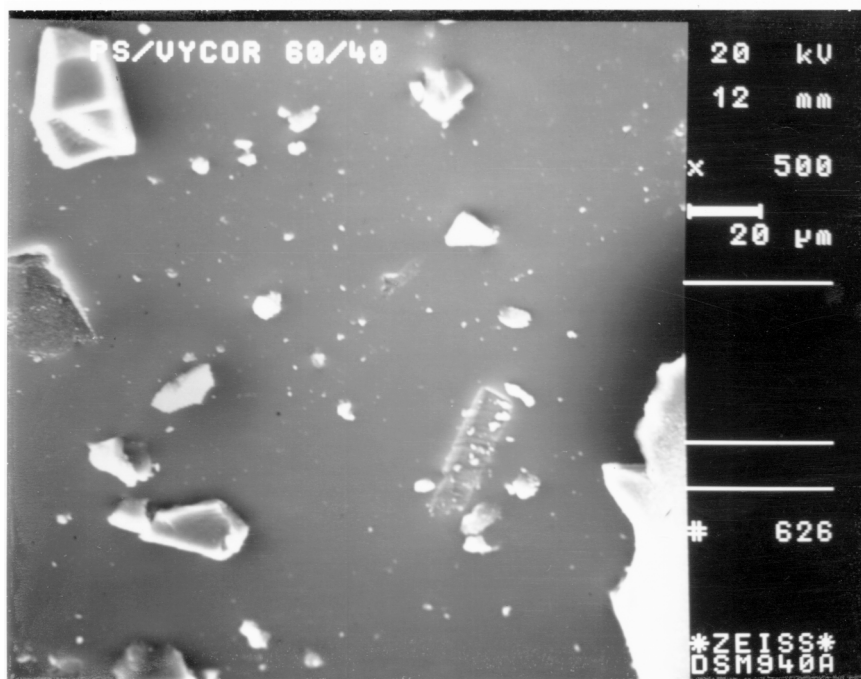
(b) Vycor-filled PS

Figure 2. Electron micrographs of (a) pure Vycor, (b) Vycor-filled PS, (c) pure zeolite 13X, and (d) PS filled with zeolite 13X.

(*continued*)

(c) pure zeolite 13X

(d) PS filled with zeolite 13X

Figure 2.   Continued.

obtained from the Corning Corporation. The pure Vycor sample studied here had smoother surface pores and showed a power-law decay of -3.54, indicating a surface fractal dimension of $d_s = 6\text{-}3.54 = 2.46 \pm 0.01$ [18]. Schaefer found that the surface fractal dimension increased with the extent of leaching. The steeper high-q slope observed here for the pure Vycor might be an indication of a different extent of leaching for the Vycor used in this study compared to that used by Schaefer [17].

Data in Figure 3 have been fitted using the unified function [19-21] with Born-Green correlations in Beaucage's modification [19-21] of the Guinier approach [22]. The fitting results in three parameters of interest, the radius of gyration for the pores R_g, the correlation distance ξ, and the power-law slope P $= d_s$ - 6 using a surface fractal model [18] (where d_s is the surface fractal dimension). Under a cylindrical pore model the radius of gyration can be related to the
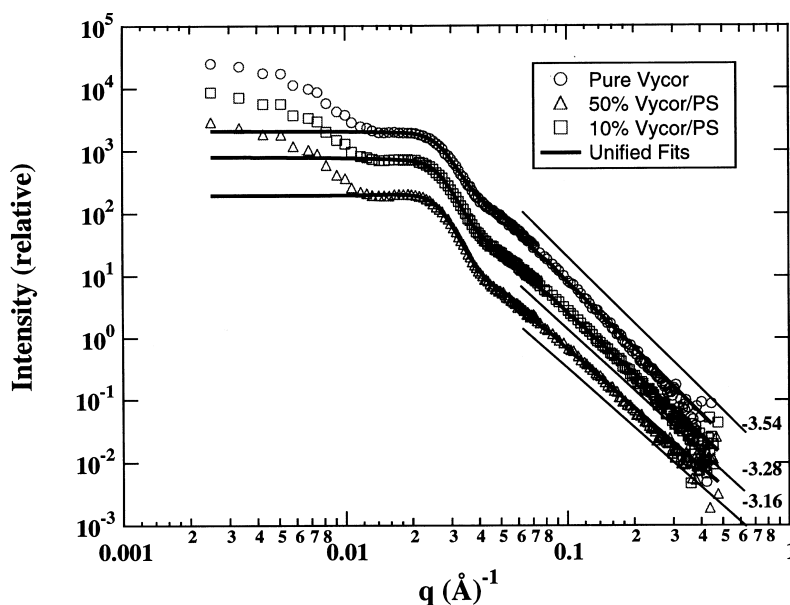

Figure 3. Scattering comparison between pure Vycor and PS filled with Vycor. Specifically, the results are given as log/log plots of relative scattered intensity versus q $[4\pi/\sin(\theta/2)]$. Scattering curves have been arbitrarily scaled on the intensity axis for clarity. The unified fittings shown as discussed in the text.

pore diameter by D = 2.31 R$_g$ [22]. Errors in the fitted values are propagated from the error in the scattered intensity through a least-squares fit using the unified function. The data in Figure 3 was fitted from q = 0.014 to 0.45 Å^{-1}, and the curves shown were recalculated using these fitted values for comparison.

In the Vycor-loaded PIPNs shown in Figure 3 the surface fractal dimension increases with loading, indicating a rougher surface with higher polymer loading; d$_s$ for 10% Vycor is 2.72 ± 0.01 and for 50% Vycor it is 2.84 ± 0.01. (For pure Vycor, d$_s$ = 2.46 ± 0.01). The increase in surface fractal dimension might result from polymer units attaching to the pore walls leading to rougher pore surfaces. Under this scenario it is expected that the pore correlation distance would remain constant while a slight decrease in the pore diameter is expected with loading depending on the extent of pore surface coverage.

The correlation distance for the pores remains fairly constant in the series: pure Vycor; 10% Vycor PIPN; and 50% Vycor PIPN: 217 ± 1; 213 ± 1 and 215±1 Å, respectively. The pore size, as measured from the radius gyration of the unified fit, decreases with Vycor loading. In the series pure Vycor; 10% Vycor PIPN, and 50% Vycor PIPN, the pore diameter D goes as: 249 ± 5 , 249 ± 2 , and 233 ± 2 Å, respectively. The value for the 10% PIPN indicates only a small degree of pore surface coverage at this lower loading level.

The scattering data is consistent with a model of polymer penetrating the Vycor pores, and roughening the pore walls by coating them. Much of the pore volume remains empty in this process since the pores are larger than the polymer chains, both in chain cross section (about 5Å) and in considering the end-to-end distance of the chains (about 50 Å). This differs from the prior results obtained on zeolite 13X composites, in which some of the pores were completely filled by polymer chains [16].

The differences in mechanical behavior between small-pore zeolites and larger-pore, leached Vycor glass could be related to the relationship between the polymer chain sizes, and pore sizes and pore volume fractions. This could be clarified by additional studies of materials of this type.

ACKNOWLEDGEMENTS

REFERENCES

[1]   R. P. Sheldon, *Composite Polymeric Materials*, Applied Science Publishers, New York, 1982.

[2]   J. E. Mark, C. Y.-C. Lee, and P. A. Bianconi, Eds*., Hybrid Organic-Inorganic Composites*, Vol. 585, American Chemical Society, Washington D. C., 1995, and relevant papers cited therein.

[3]   H. L. Frisch and J. E. Mark, *Chem. Mater., 8*, 1735 (1996), and relevant papers cited therein.

[4]   A. M. S. Al-ghamdi and J. E. Mark, *Polym. Bulletin, 20*, 537 (1988).

[5]   J. Wen and J. E. Mark, *J. Mats. Sci.,* 29, 499 (1994).

[6]   C.-G. Wu and T. Bein, *Chem. Mater., 6*, 1109 (1994); *Science, 264*, 1757 (1994); *Ibid., 266*, 1013 (1994).

[7]   R. A. Vaia, H. Islii, and E. P. Giannelis, *Chem. Mater., 3*, 1694 (1993).

[8]   P. Emzell and T. Bein, *J. Phys. Chem., 93*, 6270 (1989).

[9]   H. L. Frisch and Y. Xue, *J. Polym. Sci., Polym. Chem. Ed.,* 33, 1979 (1995).

[10]   H. L. Frisch, S. Maaref, Y. Xue, G. Beaucage, Z. Pu, and J. E. Mark, *J. Polym. Sci., Polym. Chem. Ed., 34*, 673 (1996); *Macromol Chem. Phys, 106*, 147 (1996).

[11]   H. L. Frisch, J. M. West, C. G. Goltner, and G. S. Attard, *J. Polym. Sci., Polym. Chem. Ed., 34*, 1823 (1996).

[12]   K. Morishige and K. Kawano, *J. Chem. Phys., 110*, 4867 (1999).

[13]   F. Dannusso and G. Moroglio, *J. Polym. Sci., 24*, 161 (1957).

[14]   L. H. Sperling, *Introduction to Physical Polymer Science*, 2nd Ed., Wiley, New York, 1992.

[15]   B. Erman and J. E. Mark, *Structures and Properties of Rubberlike Networks*, Oxford University Press, New York, 1997.

[16]   Z. Pu, J. E. Mark, G. Beaucage, S. Maaref, and H. L. Frisch, *J. Polym. Sci., Polym. Phys. Ed., 34*, 2657 (1996).

[17]   D. W. Schaefer, R. K. Brow, B. J. Olivier, T. Rieker, G. Beaucage, L. Hrubesh, and J. S. Lin, in *Modern Aspects of Small-Angle Scattering*, H. Brumberger, Ed., Kluwer Academic Publishers, Netherlands, 1995, p. 299.

[18]   H. D. Bale and P. W. Schmidt, *Physical Review Letters*, *53*, 596 (1984).

[19]   G. Beaucage and D. W. Schaefer, *J. Non-Cryst. Solids*, *172-174* (Pt. 2), 797 (1994).

[20]   G. Beaucage, *J. Appl. Crystallogr.*, *28* (6), 717 (1995).

[21]   G. Beaucage, T. A. Ulibarri, E. P. Black, and D. W. Schaefer, in *Hybrid
        Organic-Inorganic Composites*, 585, J. E. Mark, C. Y.-C. Lee, and P. A.
        Bianconi, Eds., American Chemical Society, Washington D. C., 1995, p.
        97.

[22]   A. Guinier and G. Fournet, *Small-Angle Scattering of X-rays*, Wiley,
        New York, 1955.