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Epoxy Networks Reinforced with Polyhedral Oligomeric Silsesquioxanes (POSS). Structure and Morphology

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ABSTRACT: Epoxy–amine networks were modified with well-defined inorganic building blocks—polyhedral oligomeric silsesquioxanes (POSS). POSS molecules were incorporated in the organic–inorganic networks as dangling units of a network chain or as network junctions. Mono- or polyepoxide POSS monomers were used to prepare the two types of networks. The structure of the POSS-containing networks, including the structure evolution during network formation, was determined by SAXS, WAXS, and TEM. The POSS pendant on a network chain shows a strong tendency toward aggregation and crystallization, depending on the POSS organic ligands. During network formation, ordering of the crystal domains takes place. The POSS–POSS interaction is the main factor controlling the network structure. Also, the polyepoxy POSSs monomers aggregate in the organic matrix; however, during network formation the system becomes more homogeneous and POSSs as network cross-links become better dispersed. Still, in the cured organic–inorganic networks the POSS junctions are slightly aggregated, and the extent of aggregation increases with decreasing POSS cross-link functionality.

Introduction

Organic–inorganic (O–I) nanocomposites are considered as a prospective material for many applications. A large class of the nanocomposites have been developed using the so-called sol–gel technique.¹ This experimental technique makes it possible to prepare composites under mild low-temperature conditions. The inorganic nanodomains of various sizes and chemical structure are formed in situ and molecularly dispersed in the organic matrix. Their formation can be controlled by reaction conditions; however, the precise control of the size and shape is difficult. Therefore, well-defined inorganic clusters are employed to prepare the O–I polymer nanocomposites with a predetermined molecular architecture. In the past decade, polyhedral oligomeric silsesquioxanes (POSS) have been used as defined molecular building blocks. POSS are clusterlike oligomers of the type $(\text{R}-\text{SiO}_{1.5})_n$, and the most common POSS compounds are cage-like derivatives $(\text{R}-\text{SiO}_{1.5})_8$ —octasilsesquioxanes (T8–POSS).² The POSS molecule is an ideal building block for synthesis of new O–I polymers, as it resembles a nanosized particle of SiO_2 . The functionalization of POSS compounds allows for their incorporation into thermoplastics without modification of existing manufacturing processes.³ One reactive functionality in the POSS cage makes it possible to prepare linear polymers or copolymers with POSS units attached as a dangling block to the polymer backbone. Such a POSS attachment to various polymers—polysiloxane,⁴ polymethacrylate,⁵ polystyrene,⁶ polyolefins,⁷ polyurethane,⁸ or polynorbornene⁹—resulted in an improvement of properties, including increased glass-transition temperature, decomposition temperature and modulus, reduced flammability, and increased gas permeability.

The incorporation of the compact nanometer-sized POSS molecule in a polymer brings about a local chain

reinforcement. The POSS units in polymers tend to aggregate or even form crystallites.^{10–12} Lichtenhan et al. suggested¹⁰ that the POSS–POSS interactions have a dominant role in controlling the resulting physical properties of modified polymers. They revealed the critical POSS concentration above which POSS–POSS interactions percolate through the system. The properties are enhanced due to formation of a physical network of the POSS continuous phase. In addition, the inter-chain interactions or inertia effect of a large mass POSS molecule is assumed to be responsible for retardation of polymer chain motion.¹¹ Theoretical simulation¹³ of the POSS–polymer system shows that aggregation of POSS moieties is not required for slowing polymer chain relaxation. The main effect of POSS is serving as an anchoring point bound to the chain. The POSS effect was also investigated in physical blends of polymers with the POSS without a covalent bonding. The low content of unbound POSS behaves like a bulky diluent, decreasing the glass transition temperature T_g .¹⁴ At high POSS contents, T_g increases due to POSS–chain and POSS–POSS interactions. The effect of bonding of POSS moieties to a polymer chain was shown by Fu et al.¹⁵ While the POSS–POSS interactions dominate in physically blended systems resulting in aggregation of POSS molecules, the POSS–polymer interaction is more important in the polymers with the chemically grafted POSS. Haddad et al.¹⁶ found that POSS covalently bound to the chain brings about a significant slowing down of chain relaxation. However, no influence on the chain mobility was observed in the system with physically blended POSS molecules. The POSS compounds represent a nanosized core–shell system with the compact POSS core and a shell of reactive or nonreactive organic substituents. The nanocomposite properties are affected by these substituents, which control the miscibility of the POSS compounds with an organic matrix. Increasing miscibility of side groups on the POSS framework results in a stronger POSS–polymer inter-

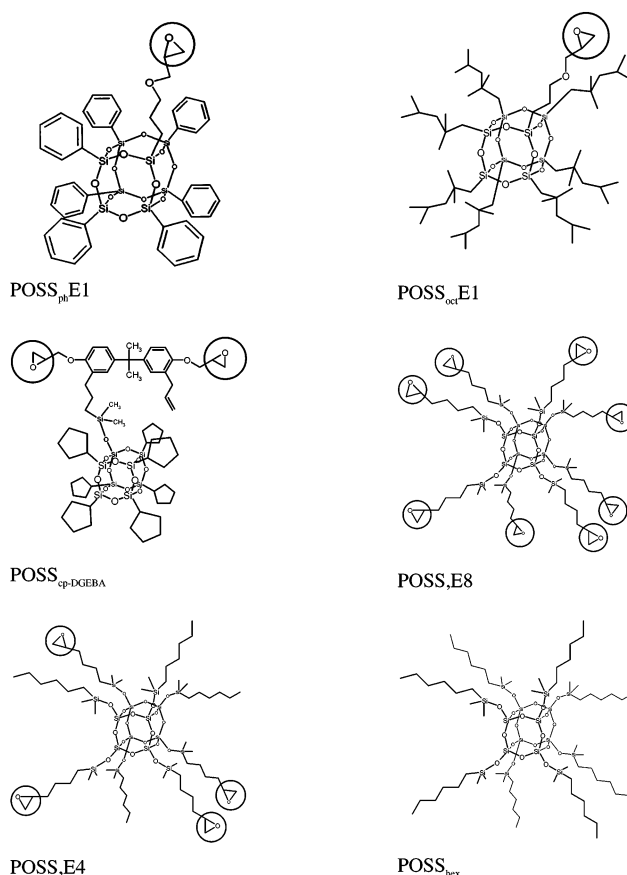
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action and an increase in T_g and modulus.¹⁷ Polyfunctional POSS cages, i.e., POSS with more reactive functional groups, are used to incorporate the POSS unit in the O–I network as a polyhedral cross-link.^{18,19} In this case, often the single-phase polymer networks with POSS molecularly dispersed are formed.^{20,21} However, at high POSS contents and a low miscibility POSS-rich nanoparticles also appear.²² In the same way as the linear O–I polymers also the O–I networks show increased modulus and thermal stability by incorporation of POSS units.

We have investigated the effect of POSS on the structure and material properties of epoxy network systems. Multifunctional epoxy-POSS monomers were synthesized in the group of Laine,^{18,23} and the octa-epoxy-POSS cage was first homopolymerized by Crivello et al.¹⁹ Photopolymerization resulted in the network with a low cross-linking density because of prevailing intramolecular reactions. Curing of polyepoxy-POSS with amines may prevent the excessive intramolecular reactions, and O–I networks of a high cross-linking density with POSS junctions are formed. Various diamines were used to tether the polyepoxy-POSS molecules; however, no definite effect of POSS on network properties was determined. Both an increase²⁰ and decrease^{24,25} in glass-transition temperature as well as no change of T_g ²¹ or even absence of a transition²⁴ were found. The POSS is well dispersed in the matrix even at a high content,²¹ and the rubbery modulus increases due to a high cross-link density.^{21,24} Less information is available from the literature about the epoxy networks with POSS units dangling on the network backbone chain. Lee and Lichtenhan²⁶ proved an increase in T_g and slowing down of the chain relaxation in the glassy state in the network diglycidyl ether of Bisphenol A (DGEBA)–butanediol diglycidyl ether–poly(oxypropylene)diamine D230 (Jeffamine) by attachment of the monofunctional epoxy-POSS. However, in the case of the monofunctional POSS phase separation occurs when POSS substituents are not compatible with the epoxy network, resulting in formation of POSS-rich domains.²⁷

In our paper the epoxy–amine network of DGEBA cross-linked with poly(oxypropylene)diamine D2000 (Jeffamine) was modified with covalently bonded or physically blended POSS units. The main goal was to determine and explain the effect of the POSS with various topological localization in a network on structure of the network in this paper and material properties in the following paper.²⁸ For this purpose we have prepared and characterized the epoxy networks with POSS incorporated as a pendant unit, as a compact block in the backbone, or as a polyhedral network junction as well as networks blended with an unbound POSS nanofiller. Moreover, as commercial POSS-epoxides show poor miscibility with DGEBA and D2000, we have synthesized POSS-epoxides highly compatible with an epoxy network. We have investigated the effect of organic substituents of the POSS framework on compatibility and final properties of the O–I network system. The POSS aggregation in the network and type of interactions, POSS–POSS and POSS–chain, controlling the structure and properties are discussed. We have followed also in situ evolution of the network phase structure during cross-linking. The structure of the POSS-reinforced epoxy networks was characterized by small-angle X-ray (SAXS), wide-angle X-ray scattering

Scheme 1. Epoxy-Functional and Nonfunctional POSS Monomers



(WAXS), and transmission electron microscopy (TEM). On the basis of the SAXS, WAXS, and TEM results, and in combination with results of dynamic mechanical analysis, the structure models of the O–I systems were proposed.

Experimental Section

Materials. The following POSS derivatives were obtained from Hybrid Plastics: POSS octasilane [octakis(dimethylsilyloxy)-T8-silsesquioxane] (Q8M8H8) and epoxy-functionalized POSS compounds; glycidyoxypropyl-heptaphenyl POSS (POSS_{ph}E1), glycidyoxypropyl-heptaisooctyl POSS (POSS_{oct}E1), and DGEBA-based POSS monomer with cyclopentyl substituents—POSS_{cp}-DGEBA (see Scheme 1). The epoxy-POSS monomers contain T8-silsesquioxane core. Poly(oxypropylene)diamine (Jeffamine D2000, molecular weight $M = 2000$) (Huntsman Inc.), diglycidyl ether of Bisphenol A (DGEBA) (SYNPO a.s. Pardubice), phenyl glycidyl ether (PGE), hex-1-ene, and 5,6-epoxyhex-1-ene (Aldrich) were used as received.

Synthesis of Multifunctional Epoxy-POSS. Multifunctional epoxy-POSS monomers with 2–8 epoxy groups (Scheme 1) were synthesized. POSS-octaepoxide (POSS_{E8}) was prepared via hydrosilylation from the octasilane Q8M8H8 and an excess of 5,6-epoxyhex-1-ene (ca. 2 C=C:1 SiH) using the Karstedt catalyst (Pt content was 4.5 ppm relative to Si–H) under an argon atmosphere at room temperature for 24 h. The octasilane is nearly insoluble in the 5,6-epoxyhex-1-ene; however, during an exothermic reaction it quickly dissolves. Excess olefin was removed under reduced pressure at room temperature. POSS-tetraepoxide (POSS_{E4}) and POSS-diepoxy (POSS_{E2}) were prepared by using a mixture of 5,6-epoxyhex-1-ene and hex-1-ene, the composition of which determined the ratio of functional and nonfunctional ligands on POSS. The purity of the POSS derivatives prepared was verified by MALDI–TOF (see Figure 1), NMR (¹H NMR δ [ppm]: 3.35, 3.16, 2.90 (epoxy group), 3.985 (–(CH₂)₃–), 1.21 (–CH₂–Si–),

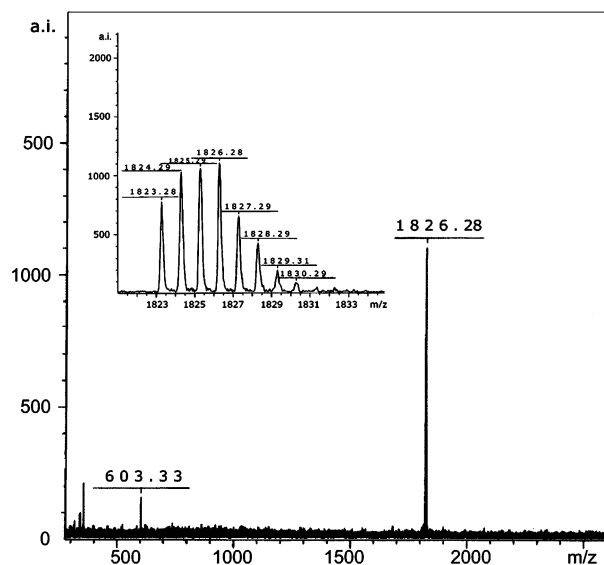


Figure 1. MALDI-TOF mass spectrum of POSS,E8. Maximum at m/z 1826.3 corresponds to $[\text{POSS,E8 Na}]^+$. Inset: isotopic distribution from 1823.3 to 1830.3.

0.72 ($-(\text{CH}_3)_2\text{Si}-$); ^{13}C NMR δ [ppm]: 51.5, 46.2 (epoxy group), 32.5, 29.8, 23.0, 17.7 ($-(\text{CH}_2)_4-$), 0.35 ($-(\text{CH}_3)_2\text{Si}-$); ^{29}Si NMR δ [ppm]: +13.0 ($-\text{Si}(\text{CH}_3)_2-\text{CH}_2-$), -108.6 ($\text{Si}(-\text{O}-)_4$) and IR spectroscopy (916 cm^{-1} (epoxy group)). The monomers POSS,E4 and POSS,E2 are statistical mixtures of a multifunctional POSS with an average functionality of 4 and 2 epoxy groups per POSS molecule, respectively. Hexyl substituents provide a good solubility of the POSS derivatives in the organic matrix. In addition, a highly soluble nonfunctional POSS (POSS_{hex}) containing hexyl substituents (Scheme 1) was synthesized by the reaction of Q8M8H8 with an excess of hex-1-ene.

Synthesis of Networks. The O-I polymer networks were prepared from DGEBA, poly(oxypropylene)diamine D2000, and the epoxy-functional POSS compounds. First, DGEBA was melted and then cooled to room temperature prior to mixing. The reaction proceeded at $120\text{ }^\circ\text{C}$ for 3 days in a Teflon mold. The reaction systems with POSS-monoepoxides POSS_{ph}E1 and POSS_{oct}E1 were not homogeneous initially and therefore they underwent ca. 30 min of reaction blending under vigorous stirring at $120\text{ }^\circ\text{C}$ prior to pouring into a mold. The less compatible POSS monomer containing cyclopentane substituents, POSS_{cp}-DGEBA, was used in the reaction as a 50% toluene solution, where the monomer was completely dissolved. The samples were cured at $100\text{ }^\circ\text{C}$ for 2 days and at $120\text{ }^\circ\text{C}$ for another 2 days (toluene evaporated under the conditions of preparation). The reaction mixtures containing liquid multifunctional epoxy-POSS monomers (POSS,En) were transparent.

Composition of the epoxy networks corresponds to a stoichiometric ratio of functional groups, $r(=\text{NH}/\text{epoxy}) = 1$. The content of POSS in the networks is characterized by weight fraction of the POSS unit, $w_{\text{POSS}} (= m_{\text{POSS unit}} / (m_{\text{POSS unit}} + m_{\text{DGEBA}} + m_{\text{D2000}}))$, where m_{DGEBA} and m_{D2000} are corresponding masses and $m_{\text{POSS unit}}$ is a mass including silsesquioxane cage and organic substituents (see Scheme 1). The POSS unit corresponds to POSS monomer except the case of POSS_{cp}-DGEBA where POSS unit does not include DGEBA part of the POSS monomer.

Methods. *Small-Angle X-ray Scattering (SAXS)* measurements were performed on a reconstructed Kratky camera with a $60\text{ }\mu\text{m}$ entrance slit and a 42 cm sample-to-detector distance. Ni-filtered Cu K α radiation ($\lambda = 0.154\text{ nm}$) was recorded with a linear position-sensitive detector²⁹ (Joint Institute for Nuclear Research, Dubna, Russia). The experimental (smeared) SAXS curves are presented as a function of the magnitude of the scattering vector $q = (4\pi/\lambda) \sin \theta$ (2θ is the scattering angle).

Table 1. POSS-Containing O-I Networks^a

<i>Network with dangling POSS</i>		
DGEBA – POSS _{ph} E1 – D2000		
DGEBA – POSS _{oct} E1 – D2000		
POSS _{cp} -DGEBA – D2000		
<i>Network with POSS in junction or backbone</i>		
POSS,E8 – D2000		
POSS,E4 – D2000		
POSS,E2 – D2000		
<i>Network with unbound POSS</i>		
DGEBA-D2000-POSS _{hex}		
● POSS unit		

• POSS unit

^a Structure of the POSS-modified epoxy networks was followed by WAXS, SAXS, and TEM.

Wide-Angle X-ray Scattering (WAXS) experiments were carried out on a powder diffractometer HZG/4A (Freiberger Präzisionsmechanik GmbH, Germany) using Ni-filtered Cu K α radiation.

Transmission Electron Microscopy (TEM) was performed with microscope JEM 200CX (JEOL, Japan). TEM microphotographs were taken at acceleration voltage 100 kV, recorded on a photographic film, and digitized with a PC-controlled digital camera DXM1200 (Nikon, Japan). Ultrathin sections for TEM, approximately 50 nm thick, were cut with ultramicrotome Leica Ultracut UCT, equipped with cryo attachment. Temperatures during cutting were -80 and $-50\text{ }^\circ\text{C}$ for the sample and the knife, respectively.

MALDI-TOF mass spectra were measured on a Biflex III instrument from Bruker; sodium acetate was the ionization agent.

NMR Spectroscopy. ^1H , ^{13}C , and ^{29}Si single-pulse MAS NMR spectra were measured using Bruker DSX 200 NMR spectrometer at the frequency of 39.75, 50.23, and 200.14 MHz for ^{29}Si , ^{13}C , and ^1H , respectively.

Results and Discussion

Various types of the epoxy networks containing POSS units (see Table 1) were prepared by modification of the epoxy-amine network DGEBA-D2000. The following types of POSS-modified epoxy networks were studied:

Networks with Pendant POSS. The networks with pendant POSS were prepared by replacing a fraction of the diepoxide DGEBA of the basic network DGEBA-D2000 with the monoepoxide-POSS monomer; POSS,E1. The monoepoxide-POSS with phenyl (POSS_{ph}E1) or isooctyl (POSS_{oct}E1) substituents was used (see Scheme 1). Another type of the epoxy networks with pendant POSS was synthesized by using diepoxide DGEBA modified with the POSS unit, POSS_{cp}-DGEBA (see Scheme 1).

Networks with POSS in Junction or Backbone. Multifunctional epoxy-POSS monomers of various functionality—octaepoxides (POSS,E8) and tetraepoxides (POSS,E4)—were used to prepare the epoxy networks containing POSS building block as cross-links of the network POSS,En-D2000. Diepoxide-POSS monomer POSS,E2 was applied for the networks with POSS unit built-in in the backbone.

Networks Filled with an Inert Unbound POSS. Nonfunctional POSS with hexyl substituents was blended with the DGEBA-D2000 system.

1. Structure of Networks with Pendant POSS. Effect of POSS Bonding to a Polymer Chain. WAXS profiles of the networks with pendant POSS blocks: DGEBA-POSS_{ph}E1-D2000 and POSS_{cp}-DGEBA-D2000 in Figure 2a show intense sharp crystalline reflections. The POSS monomers used to prepare these networks

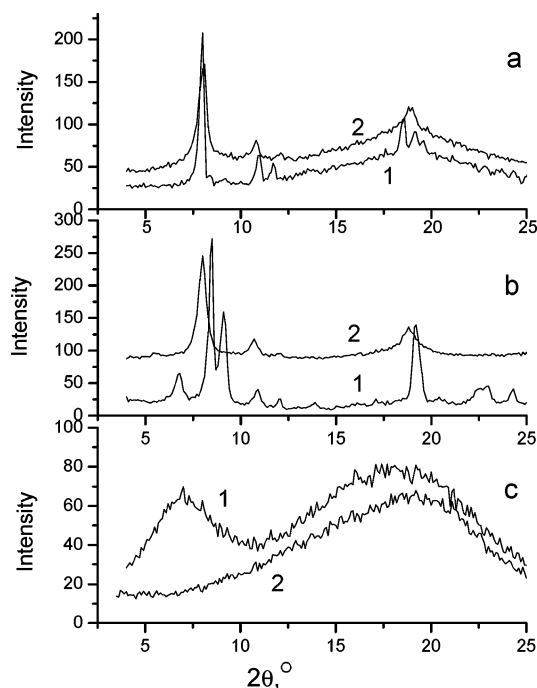


Figure 2. WAXS profiles of the (a) networks. 1: DGEBA-POSS_{ph}E1-D2000 ($w_{\text{POSS}} = 0.25$); 2: POSS_{cp}-DGEBA-D2000 ($w_{\text{POSS}} = 0.27$). (b) Monomers. 1: POSS_{ph}E1; 2: POSS_{cp}-DGEBA. (c) 1: network DGEBA-POSS_{oct}E1-D2000 ($w_{\text{POSS}} = 0.30$); 2: reference network DGEBA-D2000 ($w_{\text{POSS}} = 0$). Curves 2 are vertically shifted.

are crystalline, and the POSS crystallinity is preserved after incorporation of the POSS in the network as a dangling unit. Even a small amount of the POSS in a network ($w_{\text{POSS}} = 0.25$, i.e., 25 wt % of the POSS_{ph}E1 monomer of the total system mass), in the case of DGEBA-POSS_{ph}E1-D2000, is sufficient for crystal domains to be developed. Consequently, the results prove that cross-linking and network formation do not suppress crystallization. The question is whether the POSS crystal structure is changed after an incorporation in the network.

The diffractograms of the corresponding POSS monomers are given in Figure 2b. One can see that DGEBA-based POSS monomer (POSS_{cp}-DGEBA) possessing cyclopentyl substituents (curve 2) shows sharp peaks at $2\theta = 8.0^\circ$, 10.8° , and 18.8° . The diffractogram of the phenyl-substituted POSS (POSS_{ph}E1) (curve 1) is more complex with the main reflections at $2\theta = 8.4^\circ$, 9.1° , and 19° and a series of smaller peaks at $2\theta = 6.5^\circ$, 11° , etc. Comparison of parts a and b of Figure 2 reveals that the crystal structure of the POSS_{cp}-DGEBA unit is unaffected by incorporation in the network POSS_{cp}-DGEBA-D2000. In contrast, the structure of POSS_{ph}E1 in the network is changed and becomes similar to that in the POSS_{cp}-DGEBA-D2000 network. The two intense peaks at $2\theta = 8.4^\circ$ and 9.1° dramatically diminished, the peak at $2\theta = 6.5^\circ$ disappeared, and a new one appeared at $2\theta = 8.0^\circ$. We assume the following explanation of the fact that while the crystal structure of the POSS monomers-POSS_{ph}E1 and POSS_{cp}-DGEBA-differ (Figure 2b), their structure after attachment to the network is very similar (Figure 2a). In the POSS_{cp}-DGEBA monomer, the POSS unit is covalently attached to DGEBA (see Scheme 1), which results in steric restrictions for POSS crystallization. In contrast, POSS_{ph}E1 is a free molecule (Scheme 1) and can crystallize without any restriction leading to a different crystal structure. In

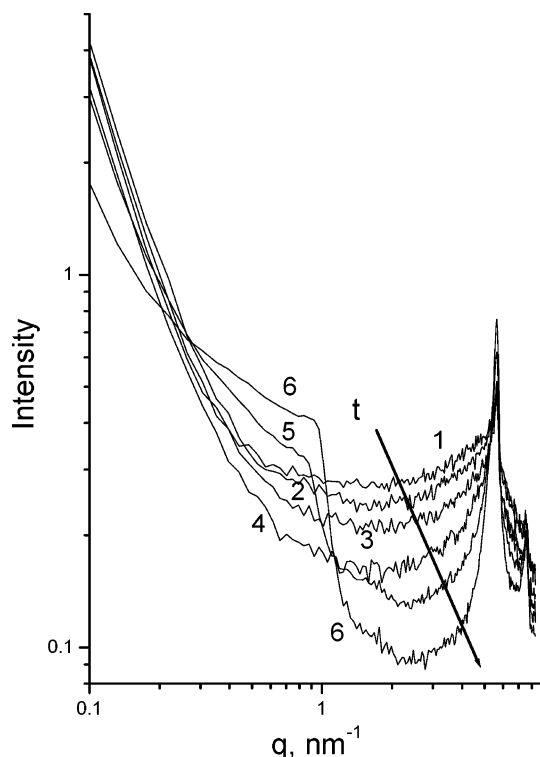


Figure 3. Evolution of SAXS profiles during formation of the network POSS_{cp}-DGEBA-D2000 ($w_{\text{POSS}} = 0.50$). Reaction time 1 $t = 0$, 6 $t = 563$ min; $T = 120^\circ\text{C}$.

the network, both types of POSS units are attached to the network chain as a pendant unit subjected to a similar steric restriction. Therefore, the POSS_{ph}E1 covalently bound to the chain behaves from the point of view of a crystalline structure similarly to the bound POSS framework in the POSS_{cp}-DGEBA. In the POSS_{cp}-DGEBA-D2000 network, there is no change of the close environment of the POSS framework on incorporation in the network because the reacting epoxy groups are relatively far from the POSS. Hence, the POSS crystal structure does not change in the network. In contrast, in DGEBA-POSS_{ph}E1-D2000, the direct bond of the POSS to the network chain through the epoxy group is formed leading to a significant restriction and modification of the structure.

Effect of Network Formation. The structure of the O-I hybrid gradually develops during cross-linking. The evolution of the structure during the formation of the POSS_{cp}-DGEBA-D2000 network was followed in situ by SAXS. Figure 3 shows two sharp peaks at $q = 5.65$ and 7.6 nm^{-1} , corresponding to WAXS region ($2\theta = 8.0^\circ$ and 10.7°) that characterizes crystallinity in the system as discussed above. One can see that, during the network formation, the X-ray scattered intensity background decreases, but the peaks positions do not change. This fact can be interpreted by a change of a distribution of POSS in the system. The higher intensity background at the beginning of the reaction is a result of scattering due to a wide dispersion of POSS in the organic matrix. During network formation the POSS units become more involved in the separated POSS domains, and the content of the dispersed POSSs decreases, leading to a drop of the background. However, the crystal structure characterized by the peak position is preserved in the network. Not even the size of the crystallites changes during the cross-linking reaching the value $L = 19.5$ nm. The crystallite size was calculated from the width

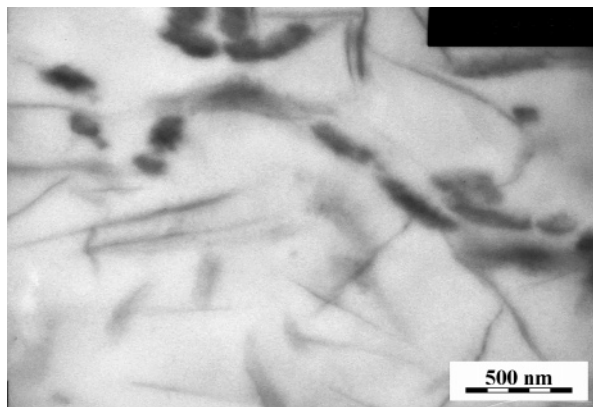
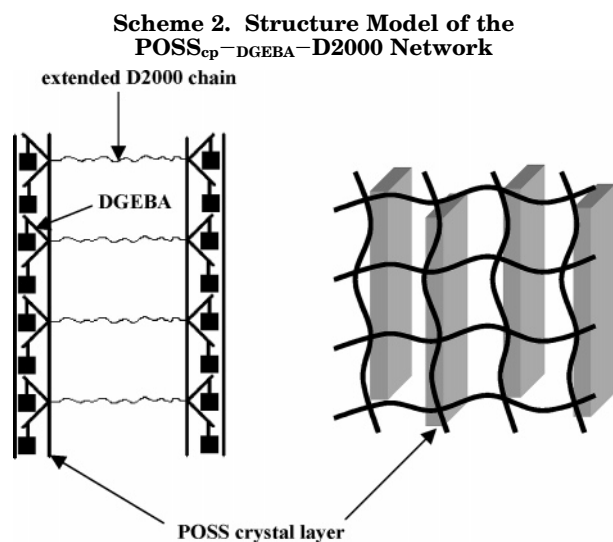


Figure 4. TEM micrograph of the POSS_{cp}-DGEBA-D2000 network ($w_{\text{POSS}} = 0.50$).



(fwhm = full width at half-maximum) of the peak at $2\theta = 8.0^\circ$ ($L = K\lambda/\beta \cos \theta$,³⁰ where $K \sim 1$, $\lambda = 0.154$ nm, and β = fwhm).

Figure 3 depicts a new SAXS maximum at $q \sim 0.8$ nm⁻¹ formed during the reaction, which reveals a gradual structure ordering in the network. This is consistent with a gradual transfer of the dispersed POSS crystallites into the separated POSS domains resulting in a decrease in intensity background discussed above. The position of the maximum corresponds to a correlation distance d ($=2\pi/q_{\text{max}}$) ~ 8 nm between the scattering objects. This distance is somewhat shorter than the contour length of D2000 chain, which is ~ 10 nm. The correlation distance depends on the length of Jeffamine molecule. We assume this is a manifestation of a regular arrangement of POSS-crystal domains separated by extended D2000 chains. This is an analogy to the organized block copolymers, where the chains are stretched along the direction perpendicular to the microdomain interface. The large size of crystallites, determined by WAXS, indicates a possible anisotropic crystallites shape with the size in one dimension being 19.5 nm. Taking into account the structure ordering found in the DGEBA-Jeffamine networks,³¹ we propose a structure model for POSS_{cp}-DGEBA-D2000 network. Scheme 2 illustrates the model involving a lamellar structure with POSS crystalline layers. The anisotropic layered structure was proved by TEM, as shown in Figure 4. More detailed study of this system will be reported in the next paper.

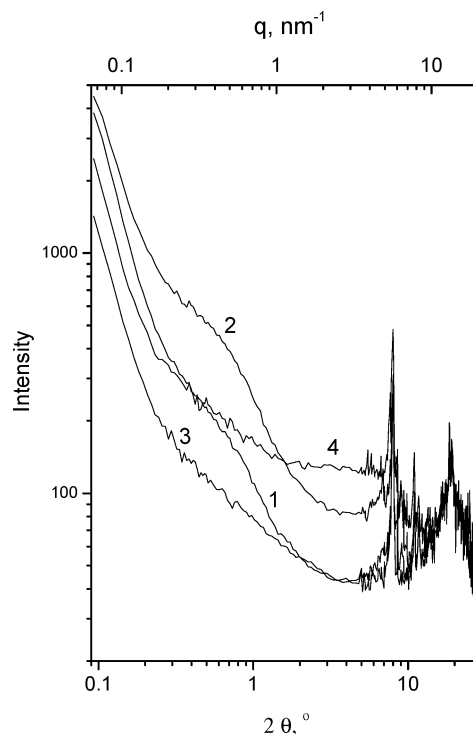


Figure 5. SAXS profiles of the DGEBA-POSS_{ph}E1-D2000 hybrid system. 1: network, $w_{\text{POSS}} = 0.25$; 2: network, $w_{\text{POSS}} = 0.48$; 3: branched polymer, $w_{\text{POSS}} = 0.25$; 4: branched polymer, $w_{\text{POSS}} = 0.60$.

Structure ordering was also observed in the DGEBA-POSS_{ph}E1-D2000 network. The shoulder at $q \sim 0.5$ nm⁻¹ in the smeared intensity profile in Figure 5 was assigned to a characteristic separation of POSS crystallites ($d \sim 12$ nm). The ordering is more pronounced and the shoulder is more distinct with increasing POSS content. Curves 1 and 2 characterize the networks with weight fraction of POSS, $w_{\text{POSS}} = 0.25$ and 0.48 , respectively. These amounts correspond to replacement of $1/3$ or $2/3$ of DGEBA molecules with POSS_{ph}E1, respectively. Consequently, not every D2000 molecule contains the dangling POSS, and therefore, the correlation distance d is larger compared to the POSS_{cp}-DGEBA-D2000 network.

The ordered structure in the DGEBA-POSS_{ph}E1-D2000 network, however, appears only in the cross-linked systems (curves 1 and 2). The branched but non-cross-linked liquid polymer containing the same weight fraction of POSS shows strong crystalline reflections in the WAXS region but no maximum in the SAXS region (curves 3 and 4). This liquid polymer was prepared using a nonstoichiometric composition with an excess of diamine D2000. In this case, a network is not formed. Consequently, the POSS crystal domains are present both in the network and in the liquid polymer, but ordering of these domains occurs only in the network. Obviously, fixing of the structure by network formation promotes regular arrangement of crystal domains of the pendant POSS units. The size of crystallites, determined from the width of the WAXS peak at $2\theta = 8.4^\circ$, is not affected by cross-linking; however, it decreases with an increasing content of POSS in the system. Both in the network and in the un-cross-linked polymer with $w_{\text{POSS}} = 0.25$, the crystallite size is $L = 37$ nm. Smaller crystallites, $L = 33$ nm, are formed in the network containing 48 wt % of POSS and in the un-cross-linked polymer with 60 wt % of POSS, $L = 27$ nm. The TEM

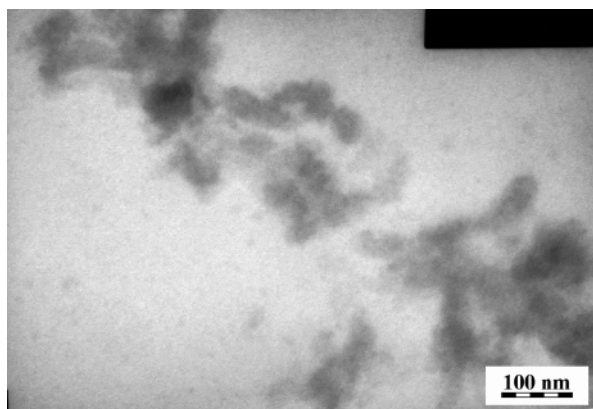


Figure 6. TEM micrograph of the DGEBA-POSS_{ph}E1-D2000 network ($w_{\text{POSS}} = 0.25$).

micrograph in Figure 6 shows an isotropic structure with more or less spherical crystal domains in contrast to the previous case.

Effect of POSS Substituents. The type of POSS substituents is crucial for compatibility with an organic matrix. Aggregation²⁷ or even crystallization of POSS occurs in the case of a poor compatibility. The monoepoxy-POSS monomer with isooctyl ligands, POSS_{oct}E1, is a liquid with no tendency to crystallize in contrast to the phenyl- and cyclopentyl-substituted POSS. Therefore, the network with the corresponding pendant POSS unit, DGEBA-POSS_{oct}E1-D2000, shows no crystallinity. Figure 2c reveals only broad amorphous maxima instead of sharp crystalline reflections. However, the compatibility with the matrix is not good enough and POSS units aggregate in the network. The broad maximum at $2\theta = 7.0^\circ$ is assumed to reflect interatomic distances within the POSS aggregates. Assignment of this maximum to a POSS structure is proved in Figure 2c. The POSS-free reference network DGEBA-D2000 (curve 2) shows an absence of the peak at $2\theta = 7^\circ$. In the case of DGEBA-POSS_{oct}E1-D2000 the characteristic distance³² ($r = 1.2\lambda/(2 \sin \theta) = 1.6 \text{ nm}$) can serve as a rough measure of the size (approximately radius) of the aggregates; diameter $2r = 3.2 \text{ nm}$. Hence, the aggregates involve only a small number (up to ~ 10) of POSS units taking into account the size of the POSS including organic ligands, $2r \sim 1.5 \text{ nm}$. Assuming close packing of POSS spheres, the size of the aggregate corresponds to ~ 7 POSS molecules.

The peak intensity at a given position is directly proportional to the number of aggregates of the corresponding size. Figure 7 illustrates that the extent of aggregation, characterized by the peak at $2\theta = 7.0^\circ$, increases with an increasing POSS content. The aggregation is similar in the network (curve 1) and in a non-cross-linked linear polymer (curve 3) containing the same amount of POSS. This fact shows that the network formation does not disturb the aggregates. In contrast to the networks with POSS crystallizing domains, no SAXS maximum was observed in the network possessing POSS with octyl ligands in Figure 7. This result proves a lack of a regular arrangement of the POSS aggregates. An upturn in intensity observed at the lowest angles of the SAXS curve of the network (curve 1) indicates the presence of larger inhomogeneities in the sample.

One has to take into account also the possibility of aggregate formation from kinetic reasons in addition to compatibility effect. The reactivity of the epoxy-POSS

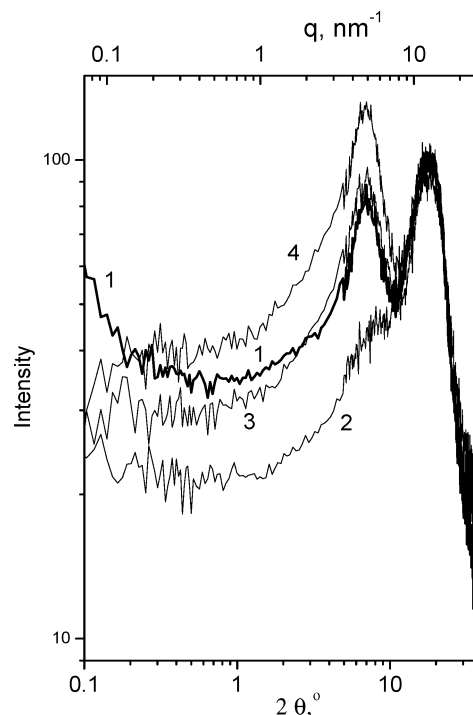


Figure 7. SAXS profiles of the DGEBA-POSS_{oct}E1-D2000 systems. 1: network, $w_{\text{POSS}} = 0.30$; 2: un-cross-linked polymer $w_{\text{POSS}} = 0.075$; 3: un-cross-linked polymer $w_{\text{POSS}} = 0.31$; 4: un-cross-linked polymer $w_{\text{POSS}} = 0.42$.

groups is lower compared to those in DGEBA. Therefore, the epoxy-amine reaction is not random and the slower incorporation of the epoxy-POSS monomers into the network may result in an inhomogeneous POSS distribution in the matrix. The effect of kinetics will be discussed in the next paper.

2. Structure of Networks with POSS as a Network Junction. The polyepoxy-POSS monomers contain hexyl ligands, POSS_{hex}En (see Scheme 1). These compounds are liquids, and the corresponding networks with POSS in a junction are amorphous, as follows from the absence of sharp crystalline reflections in the wide-angle region of the X-ray scattering profiles in Figure 8. However, a broad maximum at $2\theta = 5.5^\circ$ reveals an aggregation of POSS units in the POSS_{hex}En-D2000 networks. The diffractograms in Figure 8 are normalized to a constant content of POSS. One can see that the peak intensity at $2\theta = 5.5^\circ$ decreases with an increasing POSS functionality, implying a diminishing extent of aggregation. The highest maximum appears in the POSS_{E2}-D2000 network (curve 3), where the diepoxy-POSS is built-in into the backbone, and smaller maxima in the networks with a tetrafunctional or octafunctional POSS cross-link. The polyfunctional POSS units become shielded by D2000 chains during cross-linking. This steric shielding increases with an increasing POSS functionality and the number of D2000 chains attached by the reaction. As a result, POSSs in the backbone, POSS_{E2}, show aggregation, possibly by parallel ordering of the chains. However, an aggregation of POSS molecules forming network junctions is sterically hindered. The octafunctional POSS in the POSS_{E8}-D2000 network is relatively well dispersed in the organic matrix, as revealed by only a small interference maximum at $2\theta = 5.5^\circ$ (curve 1). The position of this broad maximum is shifted to a lower angle 2θ , compared to the networks with pendant

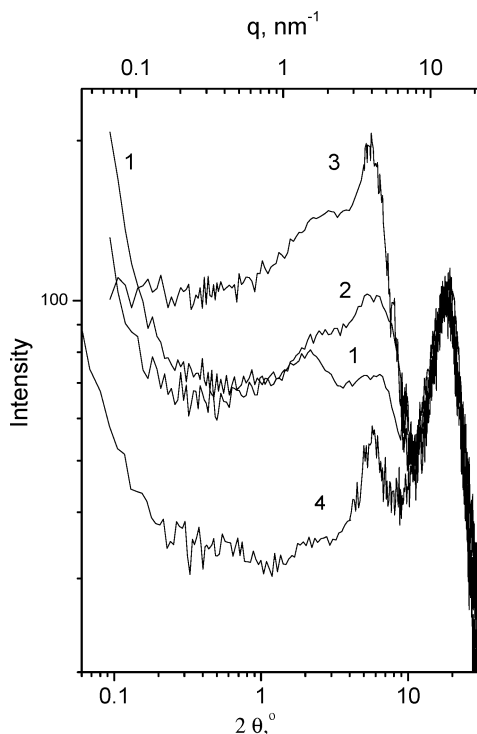


Figure 8. X-ray scattering intensity profiles of the O-I networks. 1: POSS,E8-D2000; 2: POSS,E4-D2000; 3: POSS,E2-D2000; 4: physical blend of DGEBA-D2000 with POSS_{hex}.

isooctyl-substituted POSS (cf. Figure 7), which indicates a larger size of the POSS aggregates ($2r \sim 4.0$ nm). This fact can be explained by a larger size of the POSS monomer. While the commercial POSS_{oct}E1 contains the T8-silsesquioxane core, the synthesized multifunctional POSS are based on the larger octasilane Q8M8H8 (see Experimental Section and Scheme 1).

Structure Evolution during Polymerization. The phase structure of an O-I system develops during network formation. Competition between microphase separation and the compatibilizing grafting reaction of POSS with the organic matrix govern the final structure. Early chemical bonding of the POSS to a polymer during formation of the O-I hybrid prevents phase separation due to POSS aggregation.³³ In our case, the initial reaction mixture contains the POSS_{En} aggregates, and the reaction with diamine D2000 is very slow. SAXS profiles in Figure 9 show evolution of the phase structure during formation of the POSS,E8-D2000 network. One can see that the peak at $q = 4\text{--}4.5$ nm⁻¹ (i.e., $2\theta \sim 5.5^\circ$) corresponding to the POSS aggregates gradually diminishes during the reaction. The initial aggregates are broken, and POSS molecules become more dispersed in the matrix. However, even at the end of the reaction in cured samples, there is still the small maximum corresponding to the aggregates. The POSS in cross-links are not dispersed on the molecular level in the network as reported by Lin et al.²⁰ and Li et al.,²¹ who found the POSS junctions aggregation only in the case of a very high POSS content. In our networks, the aggregates are quite small (~ 4 nm), and no large heterogeneities or microgels are formed.

At the same time the SAXS maximum in the region at $q = 1\text{--}2$ nm⁻¹ appears and grows during the reaction. The maximum gradually shifts to lower q value from $q = 1.65$ nm⁻¹ to the final value 1.24 nm⁻¹. Position of the maximum corresponds to the correlation distance, d ($=2\pi/q_{\text{max}}$) = $3.8\text{--}5.1$ nm, between POSS cages or

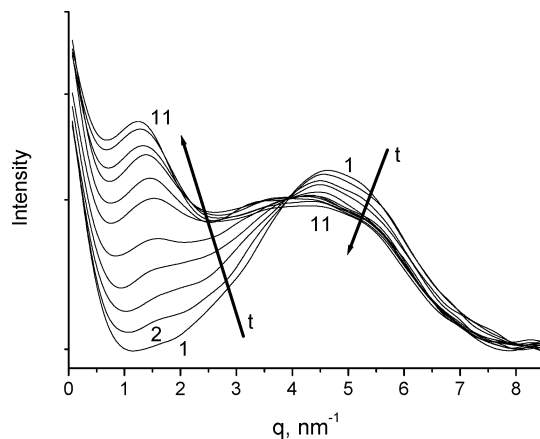


Figure 9. Evolution of SAXS profiles during formation of the network POSS,E8-D2000 ($w_{\text{POSS}} = 0.31$). Reaction time t : 1 $t = 0$, 2 $t = 2$ h, 11 $t = 90$ h; $T = 120$ °C.

aggregates of cages separated by the D2000 chain. The growth and shift of the maximum reveal formation of an ordered structure during the network buildup with an increasing distance between POSS junctions. Reaction of the octafunctional POSS,E8 with D2000 results in increasing steric restrictions around the POSS unit. Because of this overcrowded space, the D2000 chain, linking the POSS junctions, tends to be progressively more extended, thus increasing the POSS cross-links distance.

The SAXS maximum is typical of all networks with POSS in junctions or in the network backbone, POSS_{En}-D2000 as illustrated in Figure 8. The maximum of the cured network POSS,E2-D2000 (curve 3) appears at $q_{\text{max}} = 1.65$ nm⁻¹. The maximum is shifted to a lower q value and become more pronounced in the networks with a higher POSS functionality. The larger correlation distance in the cured POSS,E8-D2000 network compared to POSS,E4-D2000 and POSS,E2-D2000 is in accordance with the above explanation of space restrictions around the reacted POSS,E8 junction. In fact, structure evolution during formation of the POSS,E8-D2000 network, shown in Figure 9, corresponds to the gradual transition through the systems with increasing cross-link functionality POSS,E2-D2000 and POSS,E4-D2000, respectively. Such an analogy is proved by the SAXS results. The highest intensity of the interference maximum in the POSS,E8-D2000 network in Figure 8 (curve 1) reveals the most ordered arrangement with POSS junctions regularly separated by D2000 chains. The POSS aggregation increasing with a decreasing functionality, as determined by WAXS, results in loss of a long-range ordering. The POSS,E4-D2000 (curve 2) and POSS,E2-D2000 (curve 3) networks show broader distribution of distances between POSS units and a decrease in the SAXS interference maximum intensity. This is an analogy to the virtual decreasing conversion in the cure of the POSS,E8-D2000 system, leading to a higher extent of aggregation and lower structure ordering (see Figure 9).

Structure of Networks with Unbound POSS. A weak POSS aggregation, demonstrated by a small amorphous maximum at $2\theta \sim 5.5^\circ$ in Figure 8 (curve 4), occurs in the physical blend of the DGEBA-D2000 network with POSS_{hex} units, which are not bonded to the polymer chain. The hexyl ligands do not promote a strong POSS aggregation and the size of the aggregates

corresponds to that of POSS in junctions, as revealed by the position of the WAXS maximum. Surprisingly, there is a small SAXS interference maximum at $q = 1.7 \text{ nm}^{-1}$ in Figure 8, indicating a not well-defined correlation distance. Some interaction between POSS_{hex} units and DGEBA segments in the network could explain such an ordering.

Conclusions

The epoxy network DGEBA–D2000 was modified by compact inorganic POSS units incorporated as junctions of the network or bonded as dangling blocks of the network chain. The structure of the studied O–I networks is governed mainly by the POSS–POSS interaction within the organic matrix. The strength of the POSS–POSS interaction and propensity to aggregation in the matrix is controlled by the nature of the substituents of the POSS unit and by the topological location of the POSS in the O–I network.

The pendant POSSs aggregate and even crystallize in the network. The POSS monomers with phenyl (POSS_{ph}) or cyclopentyl ligands (POSS_{cp}–DGEBA) show a high tendency to crystallization in the organic matrix, which is not disturbed by cross-linking. Moreover, an ordering of the crystal domains takes place during the network formation. The regularly arranged POSS crystalline structures are separated by extended D2000 chains. The networks with pendant POSS having flexible isooctyl substituents are amorphous and show the presence of small POSS aggregates.

The POSS units built-in in the network as cross-links are not well dispersed in the matrix in our hybrids, in contrast to literature data.^{20,21} The homogeneity of the system increases during network formation; however, a fraction of the POSS aggregates, present in the initial reaction mixture, remains in the network. The POSS dispersion and system homogeneity increase with the increasing POSS functionality.

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References and Notes

- Brinker, C. J.; Scherer, C. W. In *Sol–Gel Science*; Academic Press: San Diego, CA, 1990.
- Bassindale, A. R.; Gentle, T. R. *J. Mater. Chem.* **1993**, *3*, 1319–1325.
- Schwab, J. J.; Lichtenhan, J. D. *Appl. Organomet. Chem.* **1998**, *12*, 707–713.
- Lichtenhan, J. D.; Vu, N. Q.; Carter, J. A.; Gilman, J. W.; Feher, F. J. *Macromolecules* **1993**, *26*, 2141–2142.
- Lichtenhan, J. D.; Otonari, Y. A. *Macromolecules* **1995**, *28*, 8435–8437.
- Haddad, T. S.; Lichtenhan, J. D. *Macromolecules* **1996**, *29*, 7302–7304.
- Tsuchida, A.; Bolln, C.; Sernetz, F. G.; Frey, H.; Muelhaupt, R. *Macromolecules* **1997**, *30*, 2818–2824.
- Hsiao, B. S.; Mather, P. T.; Chaffee, K. P.; Jeon, H.; White, H.; Rafailovich, M.; Lichtenhan, J. D.; Schwab, J. J. *Polym. Mater. Sci. Eng.* **1998**, *79*, 389–390.
- Mather, P. T.; Jeon Hong, A.; Romo-Uribe, A.; Haddad, T. S.; Lichtenhan, J. D. *Macromolecules* **1999**, *32*, 1194–1203.
- Lichtenhan, J. D.; Haddad, T. S.; Schwab, J. J.; Carr, M. J.; Chaffee, K. P.; Mather, P. T. *Polym. Prepr.* **1998**, *39* (1), 489–490.
- Romo-Uribe, A.; Mather, P. T.; Haddad, T. S.; Lichtenhan, J. D. *J. Polym. Sci., Part B: Polym. Phys.* **1998**, *36*, 1857–1872.
- Zheng, L.; Waddon, A. J.; Farris, R. J.; Farris, R. J.; Coughlin, E. B. *Macromolecules* **2002**, *35*, 2375–2379.
- Bharadwaj, R. K.; Berry, R. J.; Farmer, B. L. *Polymer* **2000**, *41*, 7209–7221.
- Xu, H. Y.; Kuo, S. W.; Lee, J. S.; Chang, F. C. *Macromolecules* **2002**, *35*, 8788–8793.
- Fu, B. X.; Gelfer, M. Y.; Hsiao, B. S.; Phillips, S.; Viers, B.; Blanski, R.; Ruth, P. *Polymer* **2003**, *44*, 1499–1506.
- Haddad, T. S.; Lee, A.; Phillips, S. H. *Polym. Prepr.* **2001**, *42* (1), 88–89.
- Phillips, S. H.; Blanski, R. L.; Svejda, S. A.; Haddad, T. S.; Lee, A.; Lichtenhan, J. D.; Feher, F. J.; Mather, P. T.; Hsiao, B. S. In *Organic/Inorganic Hybrid Materials*; MRS Vol. 628, 2000; pp CC4.6.1–CC4.6.10.
- Sellinger, A.; Laine, R. M. *Macromolecules* **1996**, *29*, 2327–2330.
- Crivello, J. V.; Malik, R. J. *Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 407–425.
- Lin, E. K.; Snyder, C. R.; Mopsik, F. I.; Wallace, W. E.; Wu, W. L.; Zhang, C. X.; Laine, R. M. In *Organic–Inorganic Hybrid Materials*; MRS Vol. 519, 1998; pp 15–20.
- Li, G. Z.; Wang, L. C.; Toghiani, H.; Daulton, T. L.; Koyama, K.; Pittman, C. U. *Macromolecules* **2001**, *34*, 8686–8693.
- Li, G. Z.; Wang, L. C.; Toghiani, H.; Daulton, T. L.; Pittman, C. U. *Polymer* **2002**, *43*, 4167–4176.
- Zhang, C.; Laine, R. M. *J. Organomet. Chem.* **1996**, *52*, 199–201.
- Choi, J.; Harcup, J.; Yee, A. F.; Zhu, Q. Y.; Laine, R. M. *J. Am. Chem. Soc.* **2001**, *123*, 11420–11430.
- Pellice, S. A.; Fasce, D. P.; Williams, R. J. *J. Polym. Sci., Part B: Polym. Phys.* **2003**, *41*, 1451–1461.
- Lee, A.; Lichtenhan, J. D. *Macromolecules* **1998**, *31*, 4970–4974.
- Abad, M. J.; Barral, L.; Fasce, D. P.; Williams, R. J. *Macromolecules* **2003**, *36*, 3128–3135.
- Strachota, A.; Kroutilová, I.; Kovářová, J.; Matějka, L. *Macromolecules* **2004**, *37*, 9457–9464.
- Chernenko, S. P.; Cheremukhina, G. A.; Fateev, O. V.; Smykov, L. P.; Vasiliev, S. E.; Zanevsky, Yu. V.; Kheiker, D. M.; Popov, A. N. *Nucl. Instrum. Methods Phys. Res., Sect. A* **1994**, *348*, 261–263.
- Scherrer, P. *Göttinger Nachrichten* **1918**, *2*, 98.
- Beck Tan, N. C.; Bauer, B. J.; Pleštil, J.; Barnes, J. D.; Liu, D.; Matějka, L.; Dušek, K.; Wu, W. L. *Polymer* **1999**, *40*, 4603–4614.
- Grenier, A. In *X-Ray Diffraction in Crystals and Amorphous Bodies*; W.H. Freeman & Co.: San Francisco, London, 1963; p 73.
- Pittman, C. U.; Li, G. Z.; Ni, H. L. *Macromol. Symp.* **2003**, *196*, 301–325.

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