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Block Copolymer Organic−Inorganic Networks. Formation and Structure Ordering

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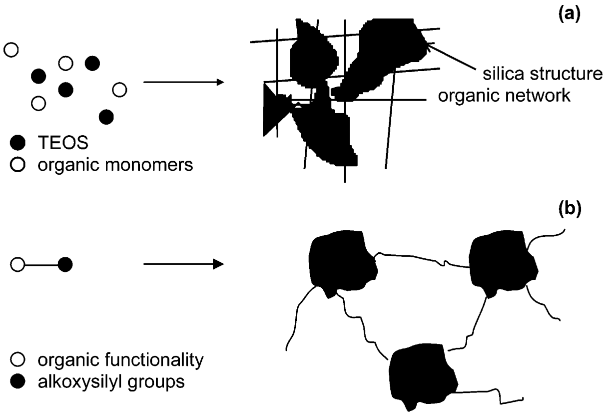
ABSTRACT: The organic−inorganic (O−I) hybrid networks were prepared from two types of O−I precursors: (a) alkoxysilane-end-capped oligomers (ASO) and (b) epoxy-functional silsesquioxane (SSQO) clusters (EC). ASO precursors were cross-linked by hydrolysis and condensation of alkoxysilane groups and the EC by the reaction of the epoxy groups with oligomeric diamine. Structure evolution and formation of the networks were followed by NMR, SAXS, and chemorheology. In addition, nongelling model systems were used to analyze the structure. Gelation mechanism and effects governing the structure evolution are discussed. Depending on catalysis of ASO polymerization, the compact SSQO cagelike structures or loose SSQO clusters are formed at the chain ends, serving as junction domains of the O−I network. In the EC−amine system, large SSQO cylinder-like domains are produced and interlinked with diamine chains. Decreasing the size or a content of the oligomeric amine results in percolation of the SSQO structure. During cross-linking a structure ordering occurs.

1. Introduction

Organic−inorganic (O−I) hybrid materials prepared by the so-called sol−gel process have been a subject of intense research in the past decade.[1−4] This process makes possible a relatively easy incorporation of a pure inorganic phase into an organic matrix. A low-temperature procedure, high purity of reactants, and possibility of mixing of precursors of organic and inorganic phases on molecular level are the main advantages of this technique. Thus, nanocomposites with a high degree of mixing can be prepared. The alkoxysilane compounds $R_{4-n}-Si(OR')_n$ are usually used as precursors of an inorganic phase formation. The "sol−gel process" consists of hydrolysis of alkoxysilanes and subsequent condensation to form linear polysiloxane $(R_2SiO)_n$ or branched and cross-linked silsesquioxane $(RSiO_{3/2})_n$ from trialkoxysilanes as well as silica $(SiO_2)_n$ structures from tetraalkoxysilanes.

Scheme 1. Organic−Inorganic Networks Formed from (a) O and I Monomers and (b) O−I Precursor



Combination of the inorganic structures with an organic matrix results in the O−I polymers that may show a synergetic combination of properties. There are several methods of preparation of O−I hybrid systems: (a) polymerization of alkoxysilanes in the organic polymer matrix,[5−7] which is the most common procedure, (b) polymerization of organic monomers in silica gel pores or impregnation of the gel with an organic polymer,[8] (c) simultaneous polymerization of organic and alkoxysilane monomers,[9] and (d) polymerization of reactants involving two types of functionalities as O−I precursors for formation of both organic and inorganic structures.[10,11] Phase or microphase separation of organic and inorganic structures is a typical feature of these systems. The hybrid morphology is determined by competition between rates of polymerization and phase separation and depends also on the interphase interaction. Physical interaction or even covalent bonding between O and I structures lead to an improvement of the system compatibility and to better mechanical properties. Therefore, coupling agents corresponding to the O−I precursors and providing a chemical bond between phases are often used to improve miscibility of the system. Common classification of O−I polymers[12] is just based on the interphase interaction and includes systems with no or weak physical interactions and polymers with the strong covalent bond between phases.

The O−I hybrid networks are a special category of O−I polymers where the matrix is constituted by a chemical or physical network of an organic or inorganic phase. In addition, a bicontinuous morphology of O and I networks can be created.[9,13,14] Two basic types of O−I networks are described in Scheme 1: (a) blend of two polymer networks produced by polymerization of organic monomers and an alkoxysilane reagent, e.g., tetraethoxysilane (TEOS), with a priori no interphase bonding; (b) O−I block copolymer network formed from O−I precursors with covalent bonds between the phases. In our previous papers[14,15] we have studied O−I networks of the first type (Scheme 1a) composed of the epoxy

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network from diglycidyl ether of Bisphenol A and poly(oxypropylene)diamine and of the silica network produced by hydrolytic condensation of TEOS. Depending on the reaction conditions, polymerization of the monomers results in formation of bicontinuous morphology or a particulate composite with silica domains dispersed within the epoxide network.

Another type of O−I network shown in Scheme 1b is produced from O−I precursors containing both organic and inorganic functionalities, e.g., organofunctional trialkoxysilanes. Their polymerization leads to the formation of an O−I block copolymer. However, often the “macromonomer”, i.e., the precursor involving an already developed organic polymer structure, is used. Alkoxysilane-end-capped polymers are typical precursors for synthesis of hybrid O−I networks.[5,6,16,17] We have applied also an opposite new approach employed much less frequently. Instead of the alkoxysilane-functionalized polymers, one can use the organic-functionalized inorganic clusters as precursors.[11,16,18]

The structure of the O−I networks is usually described by the morphological Wilkes model[6] involving an organic-rich phase matrix, dispersed inorganic-rich phase domains, and a mixed interface. The inner structure of the inorganic domains is little understood. SAXS analysis of the poly(tetramethylene oxide)−TEOS network shows[19] that the cluster domains are composed of small primary silica particles aggregated in large fractal-like clusters.

In this paper, we discuss formation of the O−I hybrid networks prepared from O−I precursors of cross-linking, as shown in Scheme 1b. The procedure consists of synthesis of a multifunctional O−I precursor of various molecular architectures and buildup of a network from the precursor. Two types of the precursors were used: the alkoxysilane-end-capped oligomer (ASO) and the inorganic silsesquioxane (SSQO) cluster with epoxy functionalities (EC).[20] The EC was cross-linked by the reaction with poly(oxypropylene)diamines. The network buildup from the organofunctional SSQO precursor has been little understood so far. In both cases, the cross-links are formed by inorganic domains linked with organic oligomer chains. However, the different synthesis approach and the precursors architecture affect the O−I network structure. Comparison of both types makes it possible to clarify the effects governing the O−I hybrid formation. Our goal is to determine structure evolution in O−I network formation and the final network structure including an inner structure of the SSQO domains dependent on the precursor architecture. Moreover, as the SSQO cluster analysis in solid networks is difficult, we investigated the structure also by using model systems. The organotrialkoxysilanes with a long organic substituent serve as low-functional models of oligomers capped with alkoxysilane groups at both ends. Because of lower functionality and the propensity to cyclization,[21] long organotrialkoxysilanes do not gel during polymerization. The soluble SSQO cluster products are more suitable for analysis than the SSQO domains in the networks. The O−I network formation, gelation, and structure evolution are followed using NMR, dynamic mechanical analysis (DMA), and SAXS.

2. Experimental Section

Materials. The trialkoxysilanes [3-(glycidyloxy)propyl]trimethoxysilane (GTMS) and (3-isocyanatopropyl)triethoxysilane (ITES) were obtained from ABCR GmbH & Co. KG. The oligomers were used for synthesis of precursors and model systems: poly(oxypropylene)diamine (D2000) and poly(oxypropylene)monoamines (M600, M2005) (Jeffamine, Huntsman Int.), poly(oxypropylene)diol (PPG2000) (Bayer, Arcol), α-hydro-ω−methoxypoly(oxyethylene) (PEO350) (Fluka), and polycaprolactone with OH end groups (PCL2000) (Aldrich). The numbers indicate approximate molecular weight of the oligomers given by the producer. M2005 was determined by MALDI−TOF to be significantly larger, $M = 2650$.

Polymerization Procedure. The hydrolysis and polycondensation of alkoxysilanes were performed using the stoichiometric amount of water, which is r_{HS} (=[H_2O]/[Si]) = 1.5 in the case of trialkoxysilanes. The reaction was catalyzed with 1 mol % of *p*-toluenesulfonic acid (TSA), dibutyltin dilaurate (DBTDL), or benzyldimethylamine (BDMA). The epoxy−amine reaction was carried out at various stoichiometric compositions of the amine and epoxy groups, r_{AE} (=[NH]/[epoxy]). The reactions were performed in bulk. Some cloudy reaction mixtures were homogenized with a small amount of isopropyl alcohol.

Methods. NMR Spectroscopy. ^{29}Si and ^{13}C NMR spectra were measured with a Bruker DSX 200 NMR spectrometer. The condensation conversion in the formation of siloxane bonds in the sol−gel polymerization of trialkoxysilanes α_{Si} was determined as $\alpha_{Si} = (\sum iT_i)/3$, where T_i indicates the fraction of the unit T_i with i siloxane bonds *Si*−O−Si− attached to the central silicon. The position of bands in the ^{29}Si NMR spectrum corresponding to T_i units was given in refs 20 and 21. ^{13}C NMR analysis was used to determine conversion of the epoxy groups.[20]

Size Exclusion Chromatography (SEC). The molecular weight distribution was characterized using a mixed-E column (Polymer Laboratories) and THF as a mobile phase. Polystyrene standards were employed for molecular weight calibration. Close agreement with the molecular weights determined by mass spectrometry of isolated fractions[20] was achieved.

Dynamic Mechanical Analysis (DMA). A rheometer ARES (Rheometric Scientific) was used to follow gelation during polymerization. Oscillatory shear deformation in parallel plates geometry at a frequency of 6.28 rad/s was applied. Also, the multiwave frequency mode was used with the frequency range of the measurement 1−64 rad/s.

Small-Angle X-ray Scattering (SAXS). SAXS measurements were performed using an upgraded Kratky camera. The measured intensities were corrected for sample thickness and transmission, primary beam flux, and sample−detector distance.

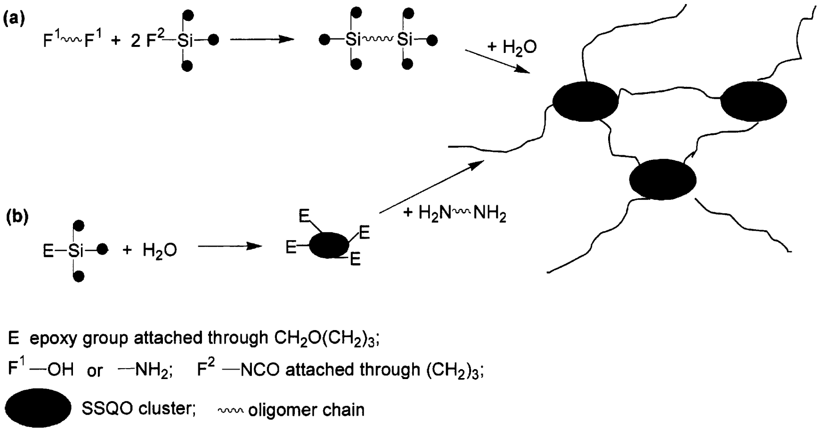
MALDI−TOF MS analyses were carried out on a mass spectrometer BIFLEX III (Bruker Daltoniks) using the reflectron mode. Solutions of the polymer in THF, the matrix (dithranol), and the cationizing agent (sodium trifluoroacetate) were mixed in the ratio 20:4:1.

3. Results and Discussion

The O−I hybrid networks are formed in two steps involving synthesis of the O−I precursors and their cross-linking. A general scheme of the O−I block copolymer network formation by two polymerization procedures from (a) alkoxysilane-end-capped oligomers (ASO) and (b) epoxy-functional SSQO clusters (EC) is shown in Scheme 2. Two reaction mechanisms operate: hydrolytic condensation of alkoxysilane groups to form SSQO domains as junctions of the O−I network and reactions of organic functionalities (epoxy + NH_2, NCO + NH_2, or NCO + OH) making the connection between these “macro-cross-links” by the organic oligomers.

3.1. Precursors of Cross-Linking. Alkoxysilane-End-Capped Oligomers (ASO). Alkoxysilane-end-capped poly(oxypropylene) or polycaprolactone of the molecular weight *x* were prepared by the reaction of

Scheme 2. Formation of the Block Copolymer O−I Networks from (a) Alkoxysilane-End-Capped Oligomers and (b) Epoxy-Functional SSQO Clusters



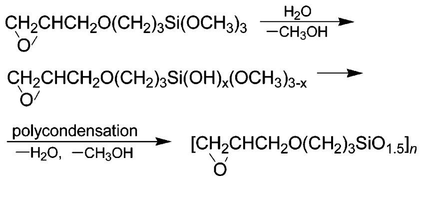
−OH- or −NH$_2$-terminated oligomers with ITES.[17]

$$\underset{\text{PPGx, PClx}}{HO\sim\sim\sim OH} + \underset{\text{ITES}}{2OCN(CH_2)_3Si(OEt)_3} \rightarrow \underset{\text{SPPGx, SPClx}}{(EtO)_3Si(CH_2)_3NHCOO\sim\sim\sim OCONH(CH_2)_3Si(OEt)_3} \tag{1}$$

$$\underset{\text{Jeffamine Dx}}{H_2N\sim\sim\sim NH_2} + \underset{\text{ITES}}{2OCN(CH_2)_3Si(OEt)_3} \rightarrow \underset{\text{SDx}}{(EtO)_3Si(CH_2)_3NHCONH\sim\sim\sim NHCONH(CH_2)_3Si(OEt)_3} \tag{2}$$

The silane-modified oligomers show a stable narrow distribution and are denoted with S−SPPGx, SDx, and SPCLx. In the case of SPPG2000 analysis of the MALDI−TOF reveals ∼7% of the mono-end-capped oligomer corresponding to an average functionality of alkoxysilane groups $f_{Si} = 5.8$ instead of the theoretical value 6. Model oligomers capped with the alkoxysilane groups at one end only were prepared in a similar way by modification of α-hydro-ω-methoxypoly(oxyethylene) (PEO350) or poly(oxypropylene)monoamines (M600 and M2005) with ITES. The corresponding models are denoted SPEOx and SMx.

Epoxy-Functional Silsesquioxane Clusters (EC). We have prepared SSQO clusters with pendant epoxy groups by hydrolysis and condensation of GTMS.[20]



$$\underset{\backslash O/}{CH_2CHCH_2O(CH_2)_3Si(OCH_3)_3} \xrightarrow[-CH_3OH]{H_2O} \underset{\backslash O/}{CH_2CHCH_2O(CH_2)_3Si(OH)_x(OCH_3)_{3-x}} \longrightarrow \xrightarrow[-H_2O,\ -CH_3OH]{\text{polycondensation}} [\underset{\backslash O/}{CH_2CHCH_2O(CH_2)_3SiO_{1.5}}]_n \tag{3}$$

Depending on the reaction conditions, we have synthesized clusters of various sizes, molecular weights (M = 500−2500), and condensation conversions α_{Si}. Using basic BDMA and DBTDL catalysts, the cyclic cagelike oligomers were preferably formed,[20] and a relatively high conversion (α_{Si} = 0.95 and 0.65−0.85, respectively) was achieved in bulk reaction at 80 °C for 1 or 3 h. On the contrary, under TSA only low conversion small SSQO oligomers (α_{Si} = 0.3−0.65) were prepared by the reaction in bulk at 20 °C for 1−4 days.

3.2. Reactions of O−I Precursors: Model Systems. For a better understanding of the cross-linking process we have first studied reactions of low-functional models.

Reaction of the Alkoxysilane-End-Capped Oligomers (ASO). Polymerization and structure evolution of ASO were modeled using organotrialkoxysilanes of various molecular weights. It was found that the reaction of long "macromonomers" SM600 and SM2005 leads to the formation of a narrow fraction of stable low-molecular- weight product only. The oligomer fraction corresponding mainly to the "macrooctamer" appears just at the beginning of the reaction,[21] and no small intermediates, "dimer" and "trimer", and no high-molecular-weight polymer are detected. ^{29}Si NMR spectroscopy reveals the distribution of the silicon T_i units in the product: $T_1 = 0$, $T_2 = 0.18$, and $T_3 = 0.82$. The total absence of T_1 characterizing chain ends of the Si units sequences and a high fraction of branched T_3 units in such a low-molecular-weight product imply highly cyclic structures. NMR analysis thus proves that the model trialkoxysilanes with a long organic substituent undergo preferentially an intramolecular condensation to form polyhedral cages. Because of steric hindrance due to the long organic chain, the intermolecular condensation is restricted and no high-molecular-weight polymer is formed. Only in the case of short SPEO350 a gradual growth of the oligomer takes place and the octamer is not formed at an early reaction stage.

Reaction of Epoxy-Functional Clusters (EC) with Amines. The clusters prepared from GTMS are not quite stable, and during cross-linking with amines the SSQO structures continue to grow. This is mainly the case of the EC formed under TSA catalysis exhibiting a low conversion α_{Si}. The basic medium of amines promotes condensation of the clusters, and hence both the epoxy−amine reactions and the sol−gel condensation take place in cross-linking of the clusters with amines. Both reactions were independently determined by model systems.

The molecular weight distribution of the EC prepared using TSA catalysis (EC/TSA) is shown in Figure 1a (curve 1). The distribution involves small oligomers ranging from dimer up to about decamer with well-resolved hydrolyzed oligomers—dimer, trimer, and tetramer. To model the "sol−gel" reaction of the cluster in cross-linking with diamines, tertiary amine BDMA was used as a catalyst. It simulates approximately basic

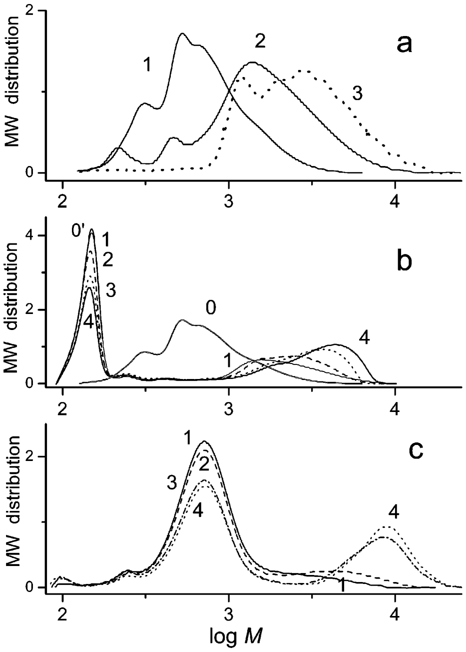


Figure 1. Evolution of the distribution of molecular weight (PS equivalent) during the reaction of the EC. (a) Sol–gel polymerization; $T = 20$ °C; 1, EC/TSA; 2, EC/TSA + BDMA, $t = 10$ min; 3, EC/TSA + BDMA, $t = 24$ h. (b) EC + DCA, $r_{AE} = 5$, $T = 25$ °C; 0, EC/TSA; 0′, DCA, 1, $t = 3$ min; 2, $t = 1$ h; 3, $t = 4.5$ h; 4, $t = 24$ h. (c) EC + M600, $r_{AE} = 5$, $T = 80$ °C; 1, $t = 10$ min; 2, $t = 30$ min; 3, $t = 3$ h; 4, $t = 24$ h.

catalytic conditions for condensation of the alkoxysilane groups while epoxy groups do not react under these conditions. BDMA initiates the fast condensation of the cluster to form immediately the product with the main fraction corresponding to the SSQO octamer cage (curve 2) with emanating (glycidyloxy)propyl groups. This product was proved by mass spectrometry,[20] and the PS equivalent molecular weight in SEC is in good agreement. Later in the reaction, other peaks become distinguished in the distribution (curve 3) assigned to polyhedral structures: cage dimer and cage trimer.[20] A basic medium was shown to advance the formation of polyhedral species. Nevertheless, finally a high-molecular-weight SSQO polymer is produced by linking the cagelike structures and the system gels.

The reaction of the epoxy groups in the EC with an amine was studied using model monoamines. The course of the reaction with decylamine (DCA) shown in Figure 1b involves both the amine addition to the epoxy groups and the cluster condensation. The initial monomers EC and DCA are characterized by curves 0 and 0′, respectively. The figure reveals that the EC disappears immediately after the reaction starts (curve 1). On the contrary, none or a very small consumption of DCA is involved during this early reaction period. The forming product corresponds to that produced in the condensation of EC catalyzed with BDMA (Figure 1a, curve 2). Obviously, as in the BDMA catalysis, the octamer cage is the main product at the beginning of the reaction of the cluster with DCA. It is the alkoxysilane condensation that dominates at early stages of the reaction in the basic medium of the primary amine. Only then a slower addition of DCA to epoxy groups of EC occurs; DCA is consumed and the product gradually grows (Figure 1b), indicating attachment of DCA to the cagelike cluster. Under conditions at a stoichiometric excess of the amine (r_{AE} = [NH]/[epoxy] = 5) shown in Figure 1b, only low-molecular-weight products are formed, and the final product distribution is stable. Excess of an amine advances full conversion of epoxy groups. Moreover, primary amine hydrogens are expected to preferentially react because of a higher reactivity of the primary amine with respect to the secondary one. Hence, an average number of reactive epoxy functionalities in the EC approximately corresponds to the attached amine molecules. As a result, the adduct ($CH_3(CH_2)_9NHCH_2CH(OH)CH_2O(CH_2)_3SiO_{3/2}$) of molecular weight $M = 324$ is the basic structure unit of the product. The peak maximum of the final distribution in Figure 1b appears at $M = 3900$, indicating functionality, i.e., the average number of epoxy groups per cluster, $f_E \sim 12$ ($\sim$3900/324). Also in the reactions of the EC with longer monoamines M600 (Figure 1c) and M2005 ($M = 2650$) stable oligomer product distributions arise with maxima at $M \sim 7500$ and 16 400, respectively, corresponding to the clusters with $f_E \sim 10$ and $f_E \sim 6$, respectively. No high-molecular-weight polymers appear. It is obvious that with increasing size of the amine smaller clusters with less epoxy groups are formed due to a shielding effect of long amine molecules emanating from the SSQO cluster and preventing intermolecular condensation. By decreasing an amine excess, however, larger clusters arise. At stoichiometric composition of the EC with M2005, a polymer of molecular weight $M \sim 30\,000$ was produced. In this case both hydrogens of the primary amino group react, and a basic structure unit is formed by an adduct: two GTMS (condensed)–M2005 of molecular weight $M \sim 2980$, containing two epoxy groups. The epoxy functionality of the cluster approaches $f_E \sim 20$ ($2 \times 30000/2980$). At an understoichiometric amount of the amine even larger structures are created, and the system finally gels. At this composition the SSQO clusters are not sufficiently shielded by the amine chains. Intermolecular condensation of the alkoxysilane groups is allowed, and the SSQO network is formed. Short amines DCA or M600 are less efficient in protecting the SSQO, and gelation occurs even at a stoichiometric composition or at a slight amine excess.

Figure 2 shows that the EC–monoamine systems are self-organized. Sharp interference maxima in SAXS intensity profiles prove a well-ordered two-phase structure of inorganic domains having a high electron density within the organic matrix. The figure reveals an effect of the amine size and its relative content r_{AE}. The position of the maximum characterizes a correlation distance between SSQO clusters and corresponds to the length of the attached amine chain separating the clusters. Increasing length of the monoamine results in a shift of the maximum in Figure 2a to a lower value of the scattering vector q. In the system EC–DCA in Figure 2b the maximum is shifted with the amount of the amine. At a high DCA excess, $r_{AE} = 5$, a sharp maximum appears at $q_{max} = 0.20$ Å^{-1} (curve 1), indicating a correlation distance given by the organic chain of DCA reacted with (glycidyloxy)propyl group. Decreasing the amine content results in a slight broadening of the peak and a shift to a higher q value. At composition with $r_{AE} < 1$ a hint of two SAXS maxima characterizing two correlation distances is shown. High deficiency of the amine ($r_{AE} = 0.2$, curve 5) brings about that most epoxy groups in the EC remain unreacted. In this case a sharp narrow maximum at $q_{max} = 0.40$ Å^{-1} dominates, and only a small shoulder at $q_{max} = 0.20$ Å^{-1} is observed.

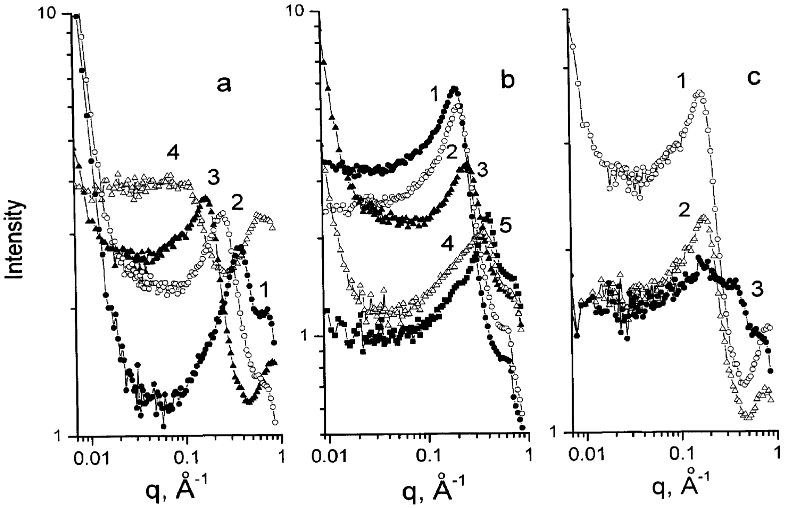
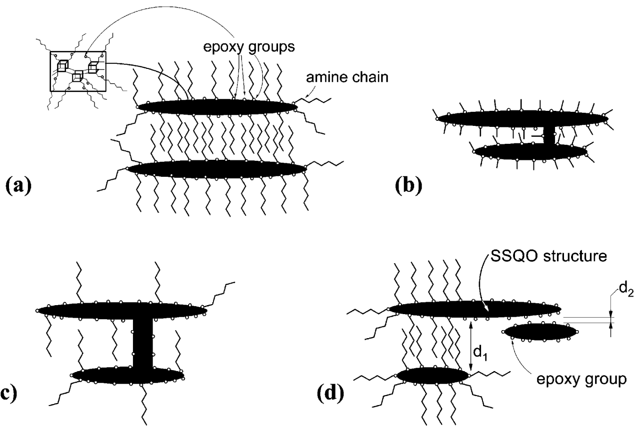


Figure 2. SAXS intensity profiles in the model systems EC–monoamine. (a) EC-amine (1, butylamine; 2, DCA; 3, M600; 4, M2005), $r_{AE} = 1$. (b) EC–DCA; 1, $r_{AE} = 5$; 2, $r_{AE} = 3.5$; 3, $r_{AE} = 1$; 4, $r_{AE} = 0.5$; 5, $r_{AE} = 0.2$. (c) EC–M600; 1, $r_{AE} = 1$; 2, $r_{AE} = 0.5$; 3, $r_{AE} = 0.2$.

Scheme 3. Structure of the EC–Monoamine System[a]



[a] (a) Long chain amine and high amine content—soluble cluster; (b) short chain amine—SSQO network; (c) small amine content—SSQO network; (d) amine deficiency $r_{AE} < 1$; two interdomain distances given by the size of the amine (d_1) and unreacted (glycidyloxy)propyl group (d_2).

The former maximum is attributed to SSQO domains separated by the unreacted (glycidyloxy)propyl groups, and it agrees with the position of the maximum of the ordered initial EC.[21] Two maxima are obvious also in the system EC–M600 at the amine deficiency in Figure 2c ($r_{AE} = 0.2$, curve 3): at $q_{max} = 0.17$ and 0.40 Å^{-1}, corresponding to the separating distance given by M600 and by (glycidyloxy)propyl groups, respectively.

On the basis of these results, we propose the following EC–monoamine structure interpretation in Scheme 3. Under basic medium of the monoamine, the EC grows by condensation of alkoxysilane groups to form larger SSQO structures composed of condensed polyhedral cages likely arranged in a cylindric shape. Addition of the monoamine only then takes place separating the SSQO clusters (Scheme 3a), thus protecting them from intermolecular condensation, and a soluble product is formed. Decreasing length of the amine chain (Scheme 3b) or decreasing the amine amount (Scheme 3c) result in a less efficient shielding of the SSQO domains. The intermolecular condensation can proceed to form "cross-bars" between the SSQO clusters, and an ordered ladderlike SSQO network structure is produced with the SSQO "cylinders" separated by dangling amine chains.

Table 1. Gelation Times t_G of the O–I Hybrid Systems at 50 °C

O–I system	t_G, min	α_c[a]	T_0[d]	T_1[d]	T_2[d]	T_3[d]
SPPG2000/TSA	5	0.26[b]	0.29	0.63	0.08	0
SPPG2000/DBTDL	600					
SPCL2000/TSA	13					
SPCL2000/DBTDL	110					
SD2000/TSA	500					
SD2000/DBTDL	160	0.19[b]	0.75	0.08	0.03	0.14
EC/TSA-D2000	74	0.20[c]	0.025	0.075	0.31	0.59
EC/DBTDL-D2000	60					

[a] Critical conversion. [b] α_{Si}. [c] α_E ($\alpha_{Si} = 0.82$ at GP). [d] Distribution of units at GP.

The composition with deficiency of an amine may result in two interdomain spacings given by the amine chain (d_1) and by the small unreacted (glycidyloxy)propyl group (d_2) (Scheme 3d).

3.3. Formation of the Hybrid O–I Networks.

Alkoxysilane-end-capped poly(oxypropylene) (SPPG2000, SD2000) and polycaprolactone (SPCL2000) were cross-linked by condensation of alkoxysilane groups (Scheme 2a). The network buildup from EC was carried out by linking the SSQO clusters with the diamine D2000 by the epoxy–amine reaction (Scheme 2b).

Gelation. Formation of the O–I networks was followed by DMA and characterized by time of gelation t_G. The dynamic modulus $G'(t)$ gradually grows during cross-linking, and at the gel point (GP) a steep increase occurs. A precise determination of the point of gelation was performed by using a power-law rheological behavior at GP,[22] taking that loss factor tan δ measured during cross-linking is independent of measurement frequency at GP. The gelation times are given in Table 1. The different O–I systems gel at 50 °C in the range 5 min–10 h depending on the type of the precursor and catalysis. The systems studied by DMA are open, and evaporation of the evolved alcohol is possible thus accelerating the reaction.

The rate of gelation of the end-capped oligomers is very sensitive to catalysis. The most convenient procedure often used is an acid/base two-step process involving acid hydrolysis followed by basically catalyzed condensation. In our one-stage polymerization the crucial reaction step was found to be hydrolysis initiating the polymerization. The acid catalysis promoting hydrolysis leads to the fast cross-linking of our open bulk systems, contrary to the closed and highly diluted systems studied by Krakovský et al.,[19] who observed a slow gelation of silane end-capped poly(tetramethylene oxide) under acid catalysis. Among the systems in Table 1, SPPG and SPCL polymerized under TSA catalysis are the quickest gelling hybrids. Hydrolysis under DBTDL or basic catalysts is slower, and gelation is substantially delayed. In addition, also internal catalytic effects operate. The urea grouping present in the SD precursor (see eq 2) is catalytically active for the "sol–gel" polymerization[21] accelerating mainly the condensation. Therefore, SD/DBTDL gels quicker than SPPG/DBTDL. The slow reaction of SD2000/TSA is caused by neutralization of the TSA with urea.[21]

The network formation from EC and diamine D2000 by the epoxy–amine reaction is slower than the cross-linking of the end-capped oligomers under the most efficient conditions. The gelation, however, is again slightly sensitive to catalysis because the "sol–gel" reaction and the EC growth also take place during cross-linking and affect the network buildup.

The rate of gelation, however, is not a direct measure of the reaction rate as it depends also on the gelation mechanism. Valuable information on the mechanism of network buildup was obtained by determination of the local structure evolution and of the critical conversion at the gel point. The critical conversion (α_c) is governed by an average functionality (f) of a system ($\alpha_c = 1/(f - 1)$ according to the classic theory of network formation) and by the reaction mechanism. For instance, a high extent of cyclization, typical of polymerization of alkoxysilanes, results in delay of gelation.[23] In the studied O–I systems one could expect two gelation thresholds corresponding to (a) the formation of the O–I block copolymer network by the epoxy–amine reaction with SSQO clusters as junction domains and to (b) the formation of the continuous SSQO network at the percolation threshold of the growing SSQO structure.

The local structure evolution during polymerization determined by ^{29}Si NMR is shown in Figure 3, and the proposed structure and gelation mechanisms are given in Scheme 4. In the case of end-capped oligomers, the cross-linking reaction mechanism is governed by catalysis. The acid-catalyzed system SPPG2000/TSA undergoes an early gelation by SSQO junction formation at conversion $(\alpha_{Si})_c = 0.26$ (Figure 3a, Table 1) with the following structure units distribution at GP: $T_0 = 0.29$, $T_1 = 0.63$, $T_2 = 0.08$, $T_3 = 0$. The theoretical critical conversion for an ideal random reaction is $[(\alpha_{Si})_c]_{th} = 0.21$, taking into account the weight-average functionality of SPPG2000; $f_{Si} = 5.8$. The evolution of structure units distribution in Figure 3a deviates from the theoretical random distribution (dotted curves 3′ and 5′). In particular, a large content of T_1 (curve 3) and a very slow growth of T_3 units (curve 5) compared to the random case reveal a strong negative substitution effect, indicating a decrease in reactivity of alkoxysilane groups after condensation of the first functional group in the monomer. Therefore, a higher experimental critical conversion could be explained in addition to a cyclization effect also by a negative substitution effect in condensation. Scheme 4a describes the structure of the system at GP. Besides unreacted T_0 units, only terminal silicon units T_1 and units T_2 of linear or cyclic SSQO structures are present at the ends of organic chains at the early stage of the polymerization up to gelation. The T_2 units at the chain ends issue three paths including two reacted functionalities Si–O– and the oligomer chain path Si–CH$_2$~~, thus forming the loose SSQO branching domain in the O–I block copolymer.

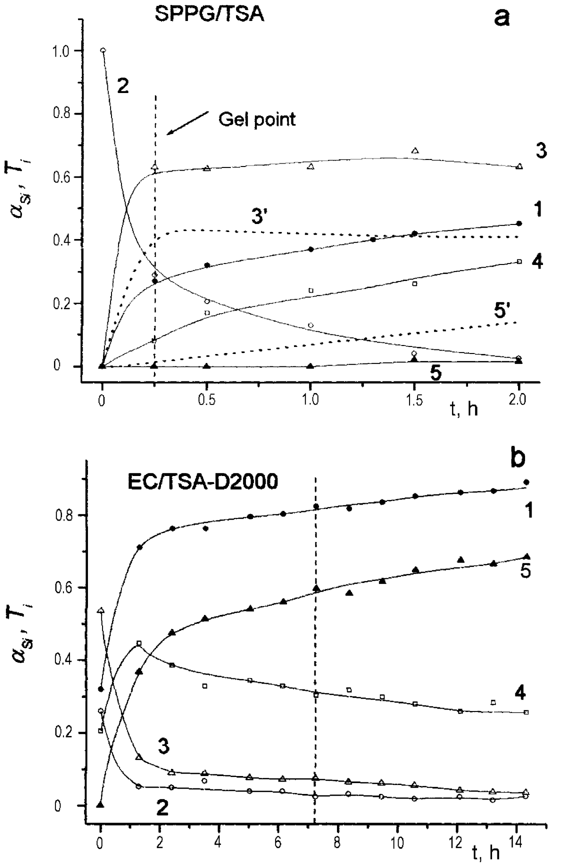
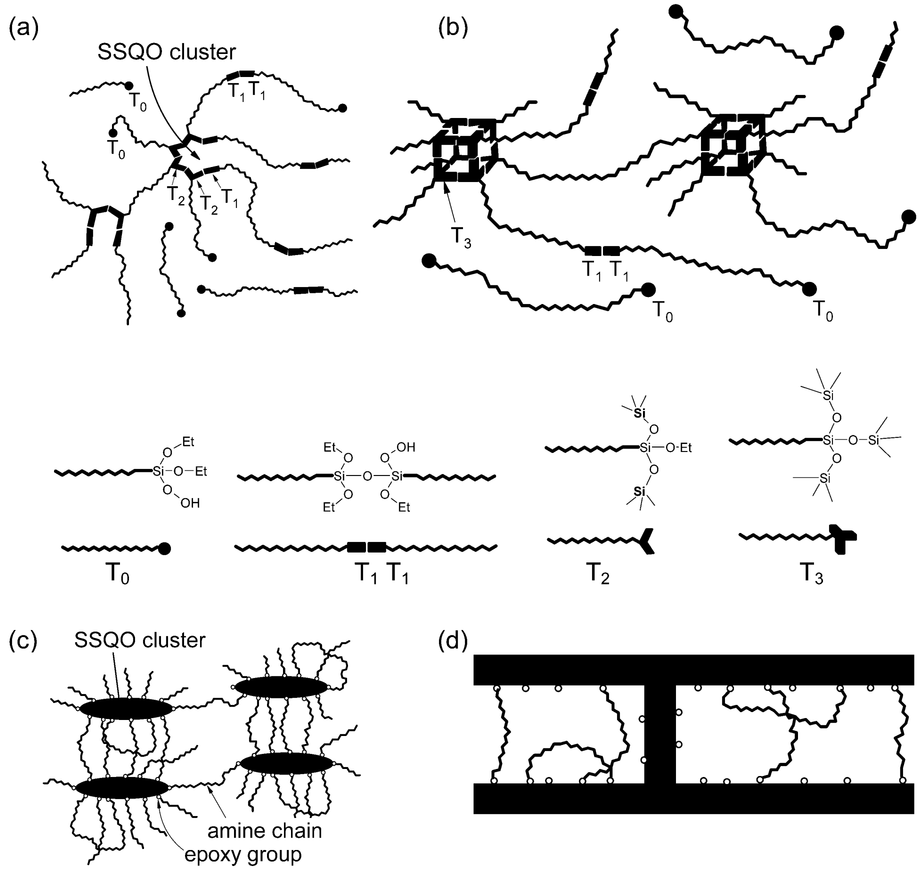


Figure 3. Evolution of conversion α_{Si} and distribution of structure T_i units during polymerization of (a) SPPG2000/TSA and (b) EC/TSA-D2000, $T = 20$ °C. 1, α_{Si}; 2, T_0; 3, T_1; 4, T_2; 5, T_3; theoretical random distribution: 3′, T_1; 5′, T_3; - - -, gel point.

The oligomer SD2000/DBTDL gels at conversion $(\alpha_{Si})_c = 0.19$. NMR analysis reveals a quite different units distribution at GP compared to the previous case (see Table 1). The main differences in evolution of both systems consist in (a) a high fraction of branched SSQO structures T_3 present in SD2000/DBTDL whereas no T_3 was detected in SPPG2000/TSA at GP and in (b) a high amount of the unreacted monomer T_0 at GP in SD2000/DBTDL in contrast to fast consumption of the monomer characterized by disappearance of T_0 in SPPG2000/TSA (Figure 3a). This fact agrees with kinetic results of the corresponding model systems. In SPEO350/TSA used as a model for SPPG2000/TSA, the gradual evolution of small oligomers (dimer, trimer, etc.) takes place while in the model system SM600 only stable SSQO cyclics, mainly octamers, were produced. The distribution of units in SD2000/DBTDL, i.e., the low content of terminal T_1 units and T_2 units, and a high content of T_3, is consistent with intramolecular branching to form small polyhedral cyclics. During polymerization T_3 appears at the early beginning of the reaction. Hence, the absence of T_2 units reveals a strong positive substitution effect and preferred formation of the "cage" with pendant alkoxysilane-terminated poly(oxypropylene) chains as building units (see Scheme 4b). The high fraction of T_0, however, shows that most of the SD2000 precursor is still unreacted at the GP. The distribution of structure units corresponds to a mole fraction of the cages $n_C =$

Scheme 4. Structure of the O–I Hybrids near the Gel Point[a]



[a] (a) SPPG2000/TSA; (b) SD2000/DBTDL and final structure; (c) EC/TSA-D2000, $r_{\mathrm{AE}} = 1$ (d)EC/TSA-D2000, $r_{\mathrm{AE}} < 1$.

0.05 at GP. Formation of cagelike precursors was assumed in the model by Rankin et al.[23] for systems with very fast cyclization. Such mechanism accounts for an extreme delay of gelation in the reaction of tetraalkoxysilanes. However, in our case of bis(trialkoxysilane)-end-capped oligomer, the cage precursor contains pendant functional chains, thus showing a very high functionality ($f_{\mathrm{Si}} = 24$; three alkoxysilane groups per each pendant chain of the octamer cage). This is the reason for a small effect of cyclization on the shift of GP and a low critical conversion. Statistical calculation for random co-condensation of the determined content of the cage and the monomer ($f_{\mathrm{Si}} = 6$) gives $[(\alpha_{\mathrm{Si}})_{\mathrm{c}}]_{\mathrm{th}} = 0.26$.

Cross-linking of the epoxy-functional cluster with diamines differs from the ASO cross-linking mainly in the fact that two independent reaction mechanisms contribute to the structure buildup. As found in the model systems, first growth of the SSQO clusters by condensation of alkoxysilane groups takes place followed by the epoxy–amine reaction. Growth of the SSQO structure in the EC–diamine system during cross-linking was proved by NMR. Figure 3b shows a fast disappearance of T_0 and T_1 units present in the initial EC and a significant increase in T_3 units before gelation. In the case of the stoichiometric EC/TSA-D2000, the gelation occurs by the epoxy–amine cross-linking (Scheme 4c) at conversion of the epoxy groups $(\alpha_{\mathrm{E}})_{\mathrm{C}} = 0.20$. The condensation conversion is quite high, $\alpha_{\mathrm{Si}} = 0.82$, at GP; however, the SSQO structure does not form a continuous phase. Such a high conversion α_{Si} and the high content of T_3 units, $T_3 = 0.59$ (see Table 1), without formation of the SSQO network indicate a strong base-catalyzed cyclization and formation of compact polyhedral SSQO. The polyhedral structures are produced at the early reaction stage as follows from instantaneous T_3 appearance (Figure 3b). The absence of the SSQO network buildup in the stoichiometric system was confirmed by using a model with the monoamine, EC-M2005. This model simulates the conditions for the "sol–gel" process in EC-D2000 while it has a reduced ability to form the epoxy–amine network due to a lower amine functionality. EC-M2005 does not gel at stoichiometric composition, thus revealing that the continuous SSQO structure is not produced. Consequently, because of the crucial role of the epoxy–amine cross-linking, the rate of gelation of EC-D2000 is determined by the size of the EC and a corresponding epoxy functionality of the cluster, f_{E}. This functionality was estimated by a method of critical mole ratio of functional groups[24] in cross-linking with excess of D2000. A description of the method is beyond the scope of this paper. The weight-average functionalities of the EC prepared under TSA and DBTDL catalysis, subsequently cured with D2000, are as follows: f_{E} (EC/TSA) = 10.5, f_{E} (EC/DBTDL) = 12.6. The larger size of the EC/DBTDL accounts for the quicker gelation compared to EC/TSA (see Table 1). At stoichiometric composition, however, larger SSQO are formed than in the case of amine excess. In the model systems it was found $f_{\mathrm{E}} \sim 20$. For random cross-linking of the stoichiometric EC-D2000 of such a high functionality ($f_{\mathrm{E}} = 20$, $f_{\mathrm{D}} = 4$), the classic theory predicts the critical conversion $[(\alpha_{\mathrm{E}})_{\mathrm{c}}]_{\mathrm{th}} = \sqrt{[(f_{\mathrm{E}}-1)^{-1}(f_{\mathrm{D}}-1)^{-1}]} = 0.13$. The higher experimental value, $(\alpha_{\mathrm{E}})_{\mathrm{c}} = 0.20$, can be explained by assuming an intramolecular reaction reducing the effective functionality, e.g., if both hydrogens of the NH_2 in D2000 react with the epoxy groups

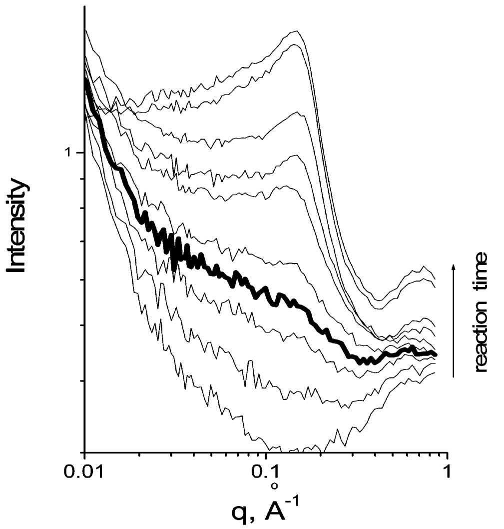


Figure 4. Evolution of intensity SAXS profiles during polymerization of SD2000/DBTDL; thick curve, gel point.

of the same cluster. In agreement with model systems we found using mechanical measurements in the next paper that in the case of deficiency of the amine the curing leads to percolation of the SSQO structure, as indicated in Scheme 4d.

Microphase Separation and Structure Ordering. During O−I network formation, microphase separation of the SSQO domains and organic polymer matrix takes place. The separation was followed by SAXS, and Figure 4 shows the evolution of the SAXS intensity profiles in the polymerization of SD2000/DBTDL. The interference maximum at $q_{max} = 0.14$ Å^{-1} indicating a regular spacing in a two-phase structure appears after the gel point and grows during the reaction. Gelation causes fixing of the ordered structure with given distances between the SSQO "cross-link points". The average spacing between domains determined by length of the organic polymer correlates with the position of the interference maximum. The conversion is relatively low at GP, $(\alpha_{Si})_C = 0.19$, implying a small electron contrast between SSQO junctions and the organic matrix. The following gradual growth of the maximum is brought about by the enhancing contrast due to increasing conversion. The peak position does not change during the reaction, indicating no or a negligible increase in the size of the SSQO cluster. The correlation distance characterized by the peak position is affected namely by the cluster size. This result is in agreement with formation of small stable SSQO oligomers and the absence of higher-molecular-weight polymers in polymerization of the models.

Structure evolution in the network formation from the EC/DBTDL and D2000 is given in Figure 5. The EC/DBTDL involving cagelike structures is self-organized,[21] and the maximum in SAXS profiles at $q = 0.40$ Å^{-1} (curve 0) corresponds to the distance between the cages. During the network buildup by the cluster growth and the epoxy−amine reaction with D2000, a new arrangement is created. Far beyond GP (curve 2) the maximum at $q = 0.135$ Å^{-1} corresponding to the length of D2000 appears and grows. Contrary to ASO, the initial mixture contains highly condensed SSQO clusters providing high contrast of electron density. Therefore, the maximum growth in this case is a result of a gradual ordering of the SSQO clusters at cross-linking with oligomeric diamine and of fixing the structure after gelation.

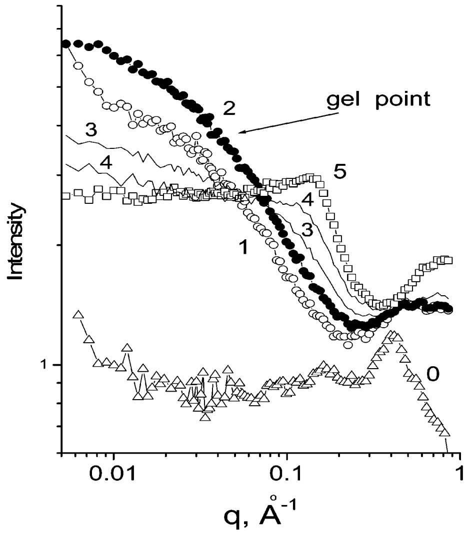


Figure 5. Evolution of the SAXS profiles during cross-linking of EC/DBTDL-D2000. Curve 0, initial EC/DBTDL; 1−5, EC + D2000. 1, $t = 0$; 2, $t = 57$ min; 3, $t = 3$ h; 4, $t = 8$ h; 5, $t = 72$ h.

4. Conclusions

We have followed formation of the O−I block copolymer based networks from two types of the O−I precursors: alkoxysilane-end-capped oligomers (ASO) and epoxy-functional SSQO clusters (EC). Cross-linking proceeded by hydrolytic condensation of terminal alkoxysilane groups in the case of ASO and the EC was interlinked by reaction with an oligomeric diamine to build the network. In both types the cross-links of the block copolymer network are formed by SSQO domains. For structure evaluation and study of the pregel evolution of the SSQO structure we have used also simple nongelling low-functional model systems.

Structure evolution and gelation of ASO are governed by catalysis. The acid catalyst accelerates hydrolysis of terminal alkoxysilane groups, which is a crucial step leading to a quick gelation of the system. Local structure analysis and the results of model systems reveal the gelation mechanism. Under acid catalysis, formation of small loose SSQO cross-link domains takes place. On the contrary, basic amine catalysts or DBTDL promote cyclization and early formation of polyhedral SSQO cages at the chain ends. These octopus-like cages with pendant functional organic chains serve as multifunctional building blocks. Cross-linking results in the network with compact cage junctions.

In the case of the EC-amine cross-linking, the SSQO cluster grows first by the condensation promoted by the amine basic catalysis. It is followed by the epoxy−amine addition that leads to linking the clusters by the organic chains and to gelation. The network formation is affected by size and relative content of the amine. Under specific conditions two percolation thresholds occur: formation of the block copolymer O−I network by the epoxy−amine cross-linking and buildup of the SSQO network by condensation of alkoxysilanes. Long oligomeric amine chains shield the SSQO structure and prevent the intermolecular condensation. However, decreasing length of the amine chain results in polycondensation and formation of large probably cylinder-like SSQO clusters. In this case finally a percolation threshold is reached, and a continuous SSQO phase is produced. The SSQO network is built up also at compositions with deficient amine chains when the SSQO clusters are less shielded.

Microphase separation takes place during polymerization and the O−I network buildup. Both systems show ordering during structure evolution which is fixed by gelation.

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