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Organization in sol–gel polymerization of methacrylate co-oligomers containing trimethoxysilylpropyl methacrylate

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Abstract

The sol–gel polymerization and resulting structures of organic-inorganic systems based on hybrid methacrylate oligomers have been studied using SEC, DSC, and SAXS. The block and random oligomers with narrow polydipersity were prepared by group transfer polymerization. All the oligomers contain 3-(trimethoxysilyl)propyl methacrylates in the chain and form silsesquioxane (SSQO) clusters by hydrolytic polycondensation, serving as cross-linking domains of the organic-inorganic network. The water miscibility and gelation of synthesized oligomers were evaluated. The systems studied can be divided into two groups—gelling and non-gelling oligomers as a result of the competition between cyclization and intermolecular reaction. The extent of cyclization and intermolecular polycondensation depends on the oligomer structure, i.e. position and number of the functional trimethoxysilyl-monomer units, and on molecular weight of the oligomeric chains. Due to the incompatibility of the SSQO framework and organic chains, microphase separation and structure ordering occur during polymerization.
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Keywords: Organic–inorganic hybrid; Sol–gel process; Oligomers

1. Introduction

The oligomers containing 3-(trimethoxysilyl)propyl methacrylates (TMSPMA) prepared by group transfer polymerization (GTP) can serve as precursors of organic-inorganic (O–I) hybrid systems. O–I materials are favorable systems for a variety of applications due to their exceptional properties based on the combination of the organic and inorganic phases [1]. An appropriate approach to the preparation of O–I hybrids is the hydrolytic polycondensation of oligomeric trialkoxysilanes, so called sol–gel process [2]. The sol–gel polymerization consists of two consecutive reactions—hydrolysis and condensation with liberation of water and alcohol. These reactions of trifunctional reagents lead to the formation of SSQO network structures. It is known that intermolecular polycondensation of organotrialkoxysilanes is accompanied by cyclization [3–7]. Fasce et al. have shown an influence of non-functional substituent (from the standpoint of the sol–gel process) on the SSQO structure, steric and charge effects or hydrogen bonding being critical for the polymerization [8]. The evolution of structure in the sol-gel polymerization of low-molecular-weight organotrialkoxysilanes $R^1Si(OR^2)_3$ strongly depends [9–11] on the type of the pendant substituent R^1. When the size of R^1 increases, cyclization is preferred. The high degree of cyclization can result in preventing gelation of the system [12]. On the contrary, in the systems with short organic substituents the intermolecular polycondensation is preferred. Such systems undergo gelation and the SSQO network is formed. The type of the catalyst of the sol–gel process is also a determining factor of behavior of the reaction system. Basic and pH-neutral catalysts support cyclization [13]. Because of mutual incompatibility of the SSQO and organic groups, the phase- or microphase separation takes place and often self-organization into micelles occurs.

In the present work we have prepared block and random copolymers based on the three co-monomers—3-(trimethoxysilyl)propyl methacrylates (TMSPMA), 2-(dimethylamino) ethyl methacrylate (DMAEMA), and isobutyl methacrylate (IBMA). We studied the influence of the position and the number of the functional TMSPMA and the molecular weight of the oligomeric chains on the structure evolution by the sol–gel process and gelation of the O–I system. The polymerization was followed by size exclusion chromatography (SEC),

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and the resulting structure was analyzed by small-angle X-ray scattering (SAXS) and differential scanning calorimetry (DSC).

2. Experimental section

2.1. Materials

All the chemicals used were purchased from Sigma-Aldrich. The monomer 3-(trimethoxysilyl)propyl methacrylate (TMSPMA) was used as received. Isobutyl methacrylate (IBMA), 2-(dimethylamino)ethyl methacrylate (DMAEMA) were dried by passing through dried alumina column. 1-Methoxy-2-methyl-1-trimethylsiloxypropene (MTDA) was used as the initiator of GTP. 1 M solution of tetrabutylammonium acetate in acetonitrile was used as a GTP catalyst.

2.2. Synthesis

2.2.1. Group transfer polymerization

The methacrylate co-oligomers were synthesized by the GTP technique in tetrahydrofurane (THF) [14]. The monomers and solvent were rid of GTP inhibitors, i.e. admixtures containing free protons, by passing through a column of dry alumina, and they were kept in cold over molecular sieves.

For the synthesis, the dry apparatus was charged with THF, initiator and catalyst under argon. This mixture was treated with the monomer added drop by drop, while the temperature of the reaction mixture was monitored throughout the exothermic reaction. After completed reaction of the components present, which was signaled by a decrease in temperature, further monomer portion was added and the procedure was repeated. In the preparation of random polymer, all monomers were introduced simultaneously. The GTP oligomers were obtained as 50 wt% solutions in THF.

2.2.2. Sol–gel polymerization

The reaction mixture of methacrylate oligomer containing trialkoxysilanes with a defined content of water was frozen, sealed in a glass ampoule and homogenized. The hydrolytic polycondensation of the oligomer proceeded in the sealed ampoule at the temperature of 40 °C. The sol–gel reaction was not additionally catalyzed because DMAEMA served as a basic catalyst.

Next phase of preparation varied depending on whether or not the sample formed a gel. The former samples, after having formed the gel, were left to stand at 40 °C for 7 days and then dried at the temperatures of 25, 50 and 80 °C for a period of 21 days. The latter samples, which did not form the gel, after reaching the equilibrium concentration, were kept at 80 °C for 20 days to complete the reaction.

The amount of water used in the sol–gel process was characterized by the molar ratio r (H_2O/Si). For the systems with trialkoxysilane groups, the stoichiometric ratio of water was $r=1.5$. The water content also includes that part which is needed for decomposition of the 'living' ends of GTP oligomers.

2.3. Methods

SEC analysis was carried out using a chromatograph produced by Waters Comp. Two columns PLgel Mixed-C were used with THF as the mobile phase and differential refractometer 410. The columns were calibrated by means of polystyrene standards. The samples were dosed as solutions in THF of 0.3–0.4 wt% concentrations in the amount of 100 μl.

Small-angle X-ray scattering measurement (SAXS) was carried out with a camera Kratky (Paar KG, Graz) with slot collimation. A rotating copper anode was the source of X-rays with the wavelength $\lambda=1.54$ Å. The intensity of scattered radiation was measured in the range of scattering vector q from 0.005 to 1.0 Å^{-1}.

Differential scanning calorimetry (DSC) was performed with the instrument Pyris 1 from Perkin–Elmer in the temperature range from -10 to 120 °C at the heating rate of 15 °C/min and the stepwise procedure (up 2 °C, down 1 °C).

The samples for determination of gel fraction were prepared in the way described in the paragraph about sol-gel polymerization for $r=3$ and $T=40$ °C. At definite time intervals, samples were taken and extracted in THF for 2 days.

3. Results and discussion

3.1. Characterization of oligomers

The GTP method was used to synthesize a series of methacrylate co-oligomers TMSPMA–DMAEMA–IBMA (T–D–I) with various molecular weights, various composition, and with various content and location of the reactive trialkoxysilanes along the chain. The GTP technique enables a good control of structure at relatively undemanding reaction conditions as compared, e.g. with the anionic polymerization; however, in spite of that it is impossible to achieve the theoretical, precisely defined structures of the oligomers given. The main drawback lies in the widening of distribution of molecular weights, which is particularly manifested with the oligomers of lower molecular weights. The characterization of the oligomers is presented in Table 1.

The basic TMSPMA monomer contains a trimethoxysilyl group, which in the presence of water undergoes hydrolytic polycondensation resulting in gradual growth, branching and cross-linking of the oligomers. The content of TMSPMA and its location in the oligomer controls the concentration and location of the methoxysilyl functional groups. These groups are bound either in the middle of the chain or at one or, as the case may be, both ends of the oligomer. Thus, e.g. sample 1 ($D_{10.1}T_2I_{8.1}$) contains two trimethoxysilyl groups inside of the chain, sample 4 ($T_{2.0}D_{10.1}I_{8.1}$) contains the group at one its end, and sample 7 ($T_{1.0}D_{9.8}I_{7.9}T_{1.0}$) contains one group at either end of the oligomeric chain. The hydrophilic DMAEMA was used to increase the miscibility of oligomers with water; besides that, amino group can act as internal basic catalyst of the sol-gel process. IBMA serves for control of molecular weight at a given content of methoxysilyl groups and for forming non-functional sequences of the polymethacrylate chain. In all

Table 1
Schematic representation of oligomers, their characterization and selected parameters of sol–gel products

No.	Composition	M_n[a]	D[b]	$W(H_2O)$[c] (wt%)	t_{gel}[d] (min)	d[e] (nm)	T_g[f] (°C)
1	$D_{10.1}T_{2.0}I_{8.1}$	3700	1.22	9.0	–	5.7	–
2	$D_{6.7}T_{2.0}I_{5.3}$	1600	1.50	10.6	–	5.2	–
3	$D_{3.4}T_{2.0}I_{2.7}$	1200	1.49	15.6	126	3.7	48
4	$T_{2.0}D_{10.1}I_{8.1}$	3600	1.24	7.4	–	7.9	–
5	$T_{2.0}D_{6.7}I_{5.3}$	1900	1.54	9.8	–	5.7	–
6	$T_{2.0}D_{3.4}I_{2.7}$	1500	1.31	15.6	45.5	4.2	62
7	$T_{1.0}D_{9.8}I_{7.9}T_{1.0}$	3600	1.19	7.5	34.5	–	57
8	${}_{rd}T_{2.0}D_{10.1}I_{8.0}$	3000	1.18	5.7	67	–	61
9	$T_{1.0}I_{17.8}T_{1.0}$	4200	1.15	1.3	360	4.8	–
10	$D_{10.2}T_{4.0}I_{6.1}$	3800	1.20	5.1	102	–	73
11	$D_{10.1}T_{6.0}I_{4.1}$	3500	1.20	0	28	–	79

[a] Number average molecular weight.
[b] Polydispersity.
[c] The mass fraction of the water miscible with 50 wt% solution of the oligomer.
[d] Gel time evaluated at $T=40$ °C and $r=1.5$.
[e] Correlation distance between SSQO domains determined by means of SAXS.
[f] Glass transition temperature.

the oligomers, the co-monomers are located in block manner, except for oligomer 8 with random arrangement of co-monomers, ${}_{rd}T_{2.0}D_{10.1}I_{8.0}$.

3.2. Miscibility of oligomers with water

The sol–gel process, i.e. hydrolytic condensation, depends on the miscibility of the system with water. In the case of the oligomers studied, the miscibility with water depends on molecular weight and composition, i.e. mutual ratios of the co-monomers and their position along the oligomer chain. The miscibility with water, characterized by the maximum fraction of water in the homogeneous mixture, is given in Table 1. It is obvious that the miscibility decreases with increasing molecular weight of the oligomer (compare, e.g. the oligomers 3, 2, 1 and 6, 5, 4, respectively). A large effect is exerted by DMAEMA, whose tertiary amino group increases the miscibility with water thanks to the formation of hydrogen bonds (compare 7 and 9). Also the position of DMAEMA within the chain affects the degree of miscibility of the oligomers with water. The amino group located at the end of chain supports the miscibility with water better than those placed inside—between the IBMA and TMSPMA blocks, which follows from the comparison of samples 1 and 4. There exists a presumption that this could be an analogy with the behavior of surfactants with amphiphilic structure combining a polar and a non-polar ends of molecule like in sample 1. In sample 4, it is possible that the amino groups are sterically shielded by adjacent bulky groups. The effect of position of amino group is decreased with decreasing molecular weight. Moreover, it was proved that the block location of amino groups, be it inside or at the ends of the chain, is more advantageous from the standpoint of achieving higher miscibility than the random arrangement (compare 8, 4 and 1). Likewise, an important factor is the content of TMSPMA units in the oligomer. Increasing concentration of hydrophobic trimethoxysilyl groups at constant molecular weight of oligomer and constant content of DMAEMA units results in a very distinct decrease in miscibility with water (compare samples 1, 10 and 11).

The miscibility of oligomer with water increases with advancing hydrolysis of methoxysilyl groups and by the influence of the methanol formed, this alcohol being usual as co-solvent [2]. The time changes in miscibility of oligomers 10 and 11, containing 4 and 6 trimethoxysilyl groups are given in Fig. 1. Particularly oligomer 10 has a tendency to fast formation of homogeneous solutions, but in a later stage, oligomer 11 exhibits a higher maximum miscibility as a result of higher concentrations of the hydroxyl groups produced by hydrolysis and of methanol. However, during the evaluation of miscibility changes of the oligomers with time, not only TMSPMA units are hydrolyzed, but they also undergo condensation, hence the experiment includes miscibility of the condensates formed.

3.3. Sol–gel polymerization of oligomers

The functional oligomers studied contain 2–6 TMSPMA units, i.e. 6–18 reactive methoxysilyl groups. In general,

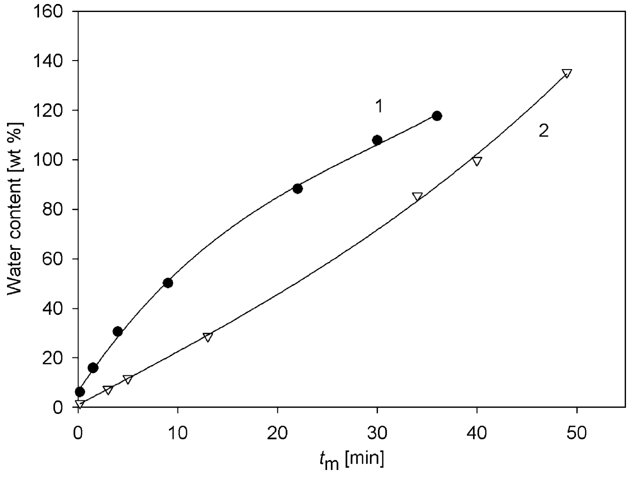

Fig. 1. Water content vs. miscibility time for oligomer 10 (1) and oligomer 11 (2).

reaction of polyfunctional reagents results in formation of branched structures, gel formation, and production of polymer network. Flory and Stockmayer derived a relationship for calculation of gelation point during ideal random reaction of an *f*-functional monomer [15]:

$$\alpha_{\mathrm{gel}} = \frac{1}{f-1} \qquad (1)$$

where α_{gel} is the conversion of functional groups at the gelation point.

For instance, for a random reaction of a six-functional monomer, the conversion in the gelation point is $\alpha_{\mathrm{gel}}=0.2$. However, hydrolytic polycondensation of polyfunctional oligomers is not a random reaction, particularly due to marked cyclization. Therefore, the gelation point is shifted towards higher conversion as compared with theory, and oligomers 1, 2, 4 and 5 do not gel at all. The ability of a polyfunctional oligomer to form a polymer network and/or the rate of formation of gel depend(s) on the structure and molecular weight of the oligomer. The gelation times, t_{gel}, characterizing the gelation rate in the reaction of the oligomers with stoichiometric amount of water, are given in Table 1. The gelation point was determined visually—by stopping the flow in the ampoule. The sol–gel polymerization of two series of oligomers 3–2–1 and 6–5–4 show that increasing molecular weight of oligomer results in the system failing to undergo gelation. The functional alkoxysilyl groups are sterically shielded by the long chain to such an extent that intramolecular reaction is preferred to the detriment of the intermolecular condensation. Therefore, with increasing molecular weight of oligomer the extent of cyclization is increased and the gelation is retarded. For a given structure, there exists a critical molecular weight M_{C} of oligomer for which the cyclization is so significant that the system does not undergo gelation. In the case of the oligomer series 3–2–1, the critical value was found in the interval of $M_{\mathrm{C}}=1200$–1600, and for series 6–5–4 it is $M_{\mathrm{C}}=1500$–1900 (Table 1).

The kinetic course of the cross-linking reaction, characterized by the gelation time, t_{gel}, depends on the reaction rate and on the reaction mechanism. In the case of strong cyclization reaction the gelation occurs only at higher conversion, as it was discussed above, and the t_{gel} value is increased. On the other hand, increasing functionality of oligomer results in decreased conversion at the gelation point (Eq. (1)) and acceleration of gel formation. The rate of hydrolytic condensation is strongly affected by the presence of DMAEMA unit. This monomer not only ensures good miscibility with water, but also acts as an internal catalyst since, in the presence of dimethylamino group, the condensation reaction of the sol–gel process is base catalyzed. The effect of DMAEMA upon the acceleration of the reaction can be seen in Table 1 if we compare the gelation times of oligomers 7 and 9 (the latter does not contain any DMAEMA unit). The presence of DMAEMA in oligomer leads to acceleration of gelation at 40 °C from 360 to 35 min. Also water concentration has an effect upon the rate of hydrolytic polycondensation. Increasing water content speeds up the hydrolysis, and the gelation times are shortened (Fig. 2).

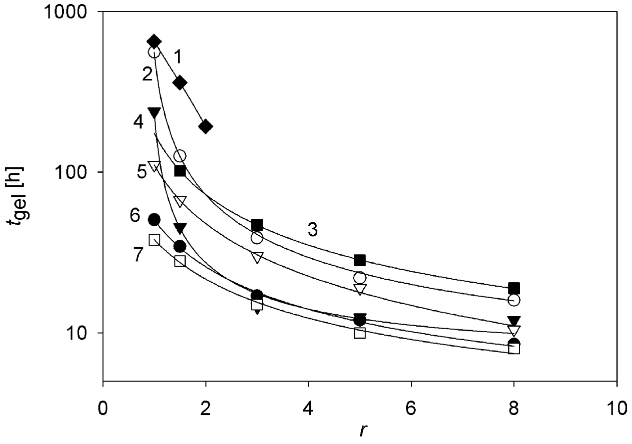

Fig. 2. Effect of ratio *r* upon gelation time of oligomeric systems. Curves: 1, oligomer 9; 2, oligomer 3; 3, oligomer 10; 4, oligomer 6; 5, oligomer 8; 6, oligomer 7; 7, oligomer 11.

The effect of number and position of functional trimethoxysilyl groups along the oligomer chain on the rate of gelation is seen from Table 1. Oligomer 6 with the functional groups at the ends of chain undergoes gelation faster than oligomer 3 with the functional groups placed inside of the chain. This effect is due to both the higher reaction rate of terminal functional groups with respect to mid-chain functional groups [16], and different reaction mechanism, because the location of groups can affect the ratio of inter- to intra-molecular reactions. Steric hindrance to the groups dangling in the middle of chain results in a lower reactivity and could lead to the preference of less demanding intramolecular reactions. The larger extent of cyclization shifts the gel point and slows down the gelation of system.

Oligomers 4, 7, and 8 have the same total composition and theoretically contain the same number of monomers in the chain. However, oligomer 7 has its functional groups at both ends of the chain, whereas in oligomer 4 the functional groups are placed at one end only. In random co-oligomer 8 the monomers are not placed in block manner but at random. Average distance between the randomly located functional groups is smaller than that in bis-trialkoxyoligomer 7, but it is larger than in oligomer 4, having both groups at one end of chain side by side. From Table 1 it follows that while oligomer 4, due to the high molecular weight and prevailing cyclization, does not undergo gelation at all, the random oligomer 8 forms gel, and the fastest gelation is found with oligomer 7. Obviously, along this sequence of systems the extent of cyclization reaction decreases and the inclination to intermolecular condensation and formation of high-molecular structures increases. It appears that the degree of cyclization, i.e. the relative ratio of intra- to inter-molecular reactions, decreases with increasing distance between the functional groups and decreasing steric hindrance in the vicinity of the functional groups. Hence the most preferred cyclization reaction is observed with the trimethoxysilyl groups placed in block manner in the middle of a chain with high molecular weight.

As expected the gelation is accelerated with increasing functionality of the oligomers in the series of systems 1, 10 and 11 with 2, 4 and 6 TMSPMA functional units, respectively.

3.4. Pre-gelation stage

The structural development of reaction mixture in the course of sol–gel polymerization was monitored by means of SEC in the pre-gelation stage, and by determination of the sol fraction, w_s, in the post-gelation stage.

Fig. 3 depict the progress in distribution of molecular weights during the reactions of the oligomers with water for $r=3$ and 40 °C in the pre-gelation stage of polymerization. The chromatograms show that in the polymerization course, the oligomers first form a bimodal distribution of molecular weights, including the non-reacted oligomer and a relatively stable low-molecular product. In the case of some of the oligomers, this product undergoes subsequent further condensation resulting in gelation of the system. However, in the case of oligomers 1, 2, 4 and 5 reacting with water, the molecular weight only increases up to an equilibrium value and no gel is formed. These equilibrium states of non-gelling systems were

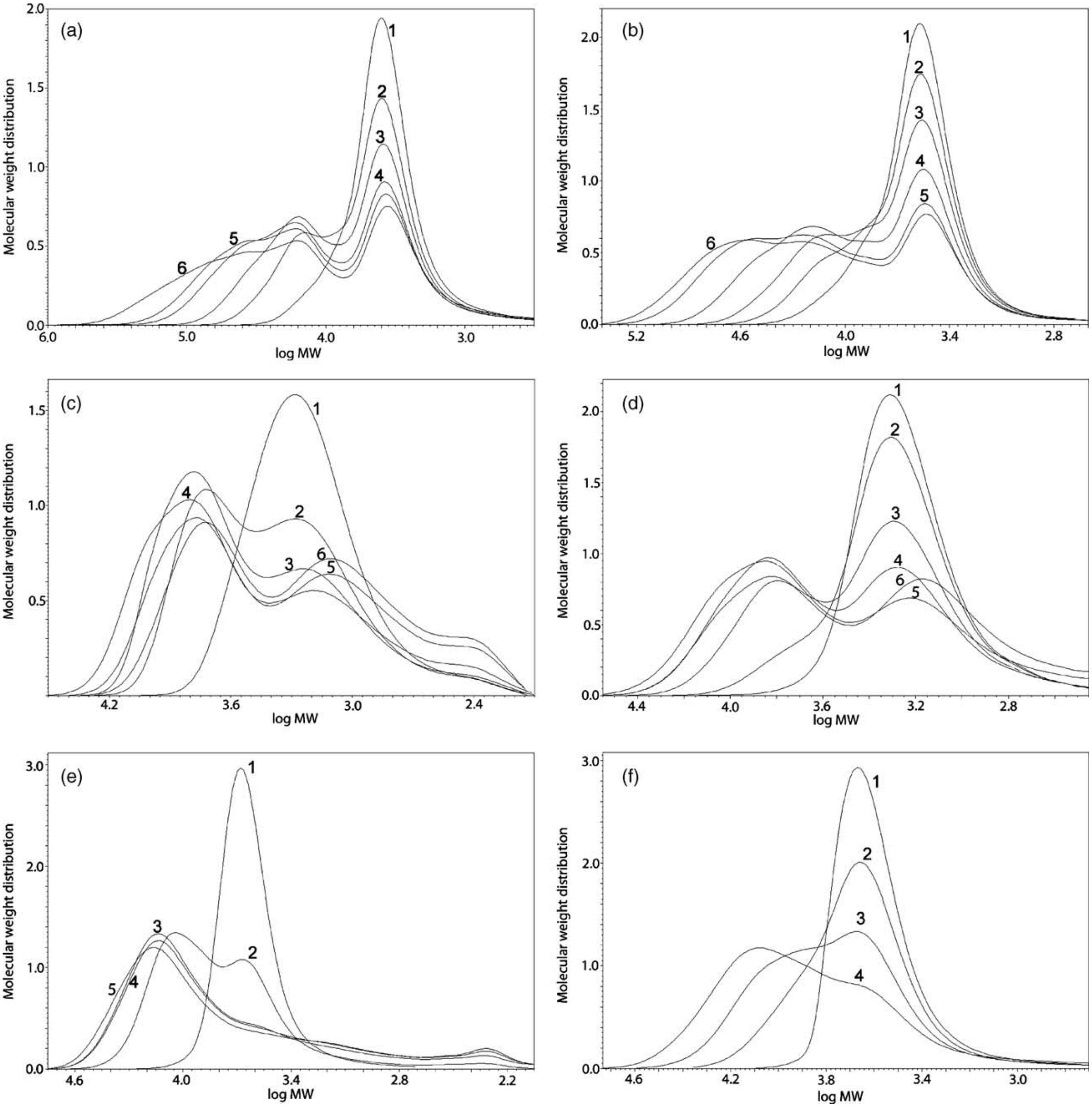

Fig. 3. Development of distribution of molecular weight during polymerization of oligomers: (a) oligomer 7, curves: 1, $t=1$ h; 2, $t=3$ h; 3, $t=5$ h; 4, $t=8$ h; 5, $t=12$ h; 6, $t=17$ h; (b) oligomer 8, curves: 1, $t=1$ h; 2, $t=3$ h; 3, $t=5$ h; 4, $t=8$ h; 5, $t=12$ h; 6, $t=17$ h; (c) oligomer 3, curves: 1, $t=1$ h; 2, $t=4$ h; 3, $t=7$ h; 4, $t=13$ h; 5, $t=22$ h; 6, $t=25$ h; (d) oligomer 6, curves: 1, $t=1$ h; 2, $t=2$ h; 3, $t=4$ h; 4, $t=5$ h; 5, $t=6$ h; 6, $t=7$ h; 7, $t=10$ h; 8, $t=12$ h; (e) oligomer 10, curves: 1, $t=0$ h; 2, $t=8$ h; 3, $t=16$ h; 4, $t=20$ h; 5, $t=32$ h; (f) oligomer 11, curves: 1, $t=0$ h; 2, $t=2$ h; 3, $t=4$ h; 4, $t=6$ h.

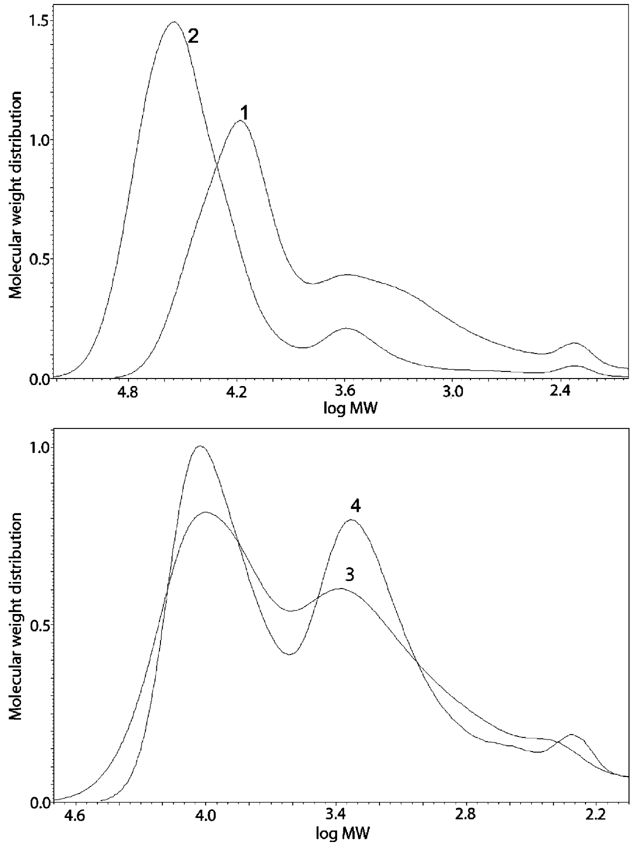

Fig. 4. Distribution of molecular weights of reacted oligomers in equilibrium states, for $r=1.5$: Curves: 1, oligomer 1; 2, oligomer 4; 3, oligomer 2; 4, oligomer 5.

evaluated by means of SEC (Fig. 4). The stable, non-reactive product probably has a cyclic structure with the functional groups having reacted in intramolecular manner. The formation of polyhedral cage-like silsesquioxanes was proved earlier [10,13,17,18]. It is just the result of formation of non-reactive cyclic products that these oligomers do not form a high-molecular polymer and network.

It was found out that the number and position of TMSPMA units, together with molecular weight of oligomer, are decisive parameters controlling not only the reaction rate and formation of gel but also the development of molecular structure and final structure of the polymer.

The distributions of molecular weights of reacted non-gelling oligomers 1 and 2 with TMSPMA units in the middle of chain exhibit maxima about $M_p \sim 16{,}000$ and $M_p \sim 9000$–10,000, respectively, which corresponds to condensation of four oligomer chains (Fig. 4). After the reaction in both systems there remains a high fraction (40–45 wt%) of the original oligomer. Such a bimodal distribution is typical of base catalyzed sol–gel process, where both higher-molecular-weight condensates and the starting macromonomer are present. Trialkoxysilyl groups of both oligomers are placed in block manner, side by side, in the middle of chain, and their accessibility for intermolecular reaction is limited. The intramolecular condensation is preferred between neighboring functional groups, which produces cycles 'pendant' on the chain, and the molecular weight is decreased mildly by splitting off of methanol. The peak of 'original oligomer' can also involve the oligomer with pendant cycles. A small peak with the maximum $M_p \sim 200$ (Figs. 3(c) and (e) and 4) has probably its origin in the decomposed (hydrolyzed) 'living' ends of oligomers. The decomposition produces hydroxytrimethylsilane, which can be further condensed to give $(CH_3)_3SiOSi(CH_3)_3$ structure with the molecular weight of 162 g mol^{-1}.

Oligomer 3 with subcritical molecular weight already forms a polymer network. The development of molecular weights shown in Fig. 3(c) again exhibits distinct bimodal shape with the maximum molecular weight detected about $M_{max} \sim 30{,}000$. The polymerization course shows an obvious gradual decrease of the original oligomer and formation of low-molecular-weight product with the maximum about $M_p \sim 6300$, which means a connection of predominantly 3–4 oligomeric chains. Before the gelation point, the distribution shifts towards lower molecular weights as a result of gradual formation of non-detectable high-molecular-weight fractions. The fraction with the highest molecular weight M_{max} near the gelation point is not detected. A large part of analyzed sample already is in the form of structures with high molecular weights, and these remain either on the filter during purification of the sample before its injection into the column or in the column itself.

In the oligomer 2, unlike 1, the functional block TMSPMA is placed at the end of chain (Fig. 4). This change affects the resulting structure of product: a larger stable product is formed, characterized by a peak with the molecular weight maximum in the interval $M_p \sim 32{,}000$–35,000: this represents formation of products probably cyclics by combination of about eight oligomeric units. In this case, the peak of non-reacted oligomer and/or the oligomer with small cycles on chain amounts only about 15 wt%.

Oligomer 5 of $M_p \sim 3{,}000$ forms cyclic products of $M_p \sim 11{,}000$ (Fig. 5). It means the tendency to predominant formation of tetramers. There appears to be a trend to dependency of distribution upon r in Fig. 5. The amount of free oligomers varies from 40 wt% for $r=1$, through 50 wt% for $r=1.5$ up to 60 wt% for $r=3$.

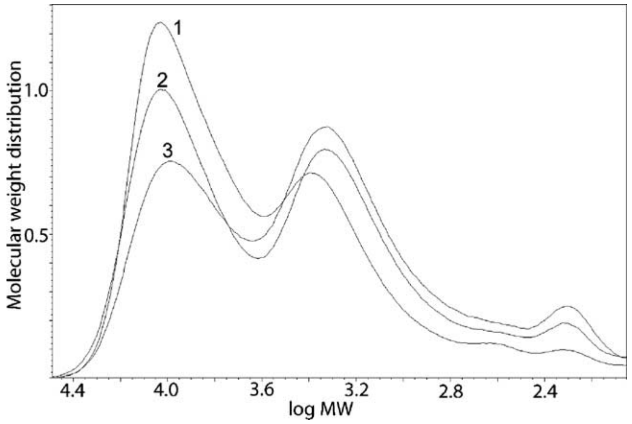

Fig. 5. Distribution of molecular weights of the oligomer 5 in equilibrium states. Curves: 1, $r=1$; 2, $r=1.5$; 3, $r=3$.

The development of structure of gelling oligomer 6 with subcritical molecular weight is given in Fig. 3(d). The course is similar to that of oligomer 3.

The oligomers 7 and 8, in which the functional groups are more distant from each other, differ markedly from the block oligomers in the development of distribution of molecular weights during the polymerization. As already discussed above, these oligomers better undergo intermolecular condensation, form high-molecular-weight polymers, and more rapidly undergo gelation at a given molecular weight and functionality (Table 1). Fig. 3(a) shows that during the polymerization of oligomer 7, again the first step is the formation of products with $M_{\mathrm{p}} \sim 17{,}000$, which in average represent a connection of approximately four oligomers. However, in the next phase of reaction the distribution extends in the direction of higher molecular weights. At the time $t \sim 5$ h, there forms a third, less distinct peak, reaching its maximum at $M_{\mathrm{p}} \sim 36{,}000$ and representing structures formed by combination of up to eight oligomers. The maximum detected molecular weight is $M_{\max} \sim 600{,}000$. From the standpoint of distribution of molecular weights, the reaction of random oligomer 8 has a similar course (cf. Fig. 3(b)).

Oligomers 10 and 11 contain 4 and 6 TMSPMA units, respectively. The increase in functionality speeds up the formation of network, and compared to the systems with two TMSPMA units (Fig. 4, curve 1), in this case the majority of the original oligomer reacts even before the gelation point (Fig. 3(e) and (f)).

The analysis of SEC results shows that in the polymerization course predominantly 3–8 oligomer chains are connected to form cyclic products. At certain conditions, these products undergo intermolecular condensation to produce high-molecular-weight structures, which, however, cannot be detected by means of SEC.

3.5. Post-gelation stage

After the gel point, the fraction of the sol, w_{s}, quickly decreases (Fig. 6). The determination of the sol fraction, however, gives only approximative values. In the course of extraction in THF, the reaction continues, despite the high dilution with a solvent, and w_{S} decreases. The sol fraction involves, in addition to the unreacted oligomer and the polymer products unattached to the network, also methanol, water and the product formed by decomposition of the active terminal of GTP oligomer.

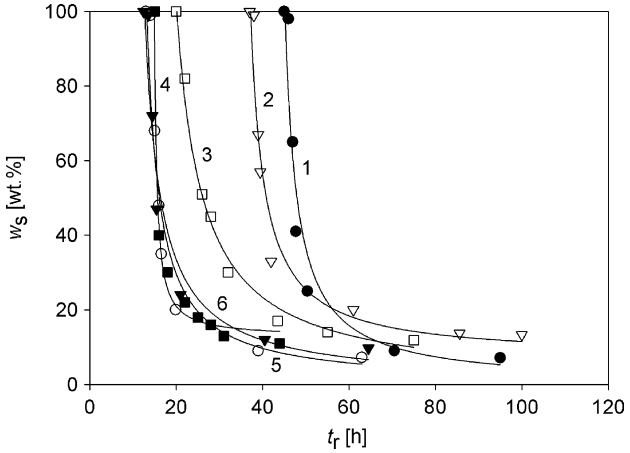

Fig. 6. Development of sol fraction, w_{s}, during polymerization of the oligomers. Curves: 1, oligomer 10; 2, oligomer 3; 3, oligomer 8; 4, oligomer 7; 5, oligomer 11; 6, oligomer 6.

3.6. Phase structure

During polymerization microphase separation of organic and inorganic structures of the hybrid polymer takes place. The phase structure of the reacted oligomers was followed by means of SAXS. The SAXS profiles of reacted oligomers in Figs. 7 and 8 exhibit two maxima, which are assigned to the intra- and intermolecular interference. The position of the maximum characterizes the correlation distance d in the system, $d(=2\pi/q_{\max})$.

A distinct maximum at about $q \sim 5\ \mathrm{nm}^{-1}$ probably corresponds to intramolecular correlation distances characterizing the inner structure of the resulting SSQO domains. The SAXS results reveal a shift of the maximum to a lower q value in the non-gelling oligomers measured in 50 wt% THF solution, $q_{\max} \sim 4.5$–$4.7\ \mathrm{nm}^{-1}$ (cf. Fig. 7) with respect to the cross-linked systems showing the maximum at $q_{\max} \sim 5.2$–$5.4\ \mathrm{nm}^{-1}$ (Fig. 8). The shift is caused by the swelling of the SSQO structures in the solvent, which results in an increase in correlation distances.

The second maximum at the lower angles (at $q \sim 0.8$–$2.5\ \mathrm{nm}^{-1}$) is given by intermolecular interference and indicates a regular arrangement of the SSQO structures in the system. The correlation length d describes the distance between the scattering SSQO domains. Fig. 7 shows that this maximum is distinct in the case of non-gelling oligomers, but it is very small with the cross-linked systems (Fig. 8). We suppose that the reacted non-gelling oligomers form micellar structures with

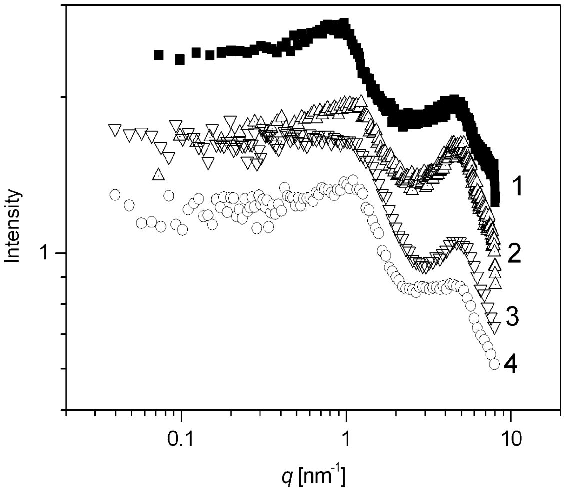

Fig. 7. SAXS profiles of polymerization products of non-gelling oligomers for $r=1.5$. Curves: 1, oligomer 4; 2, oligomer 1; 3, oligomer 2; 4, oligomer 5. Curves are vertically shifted.

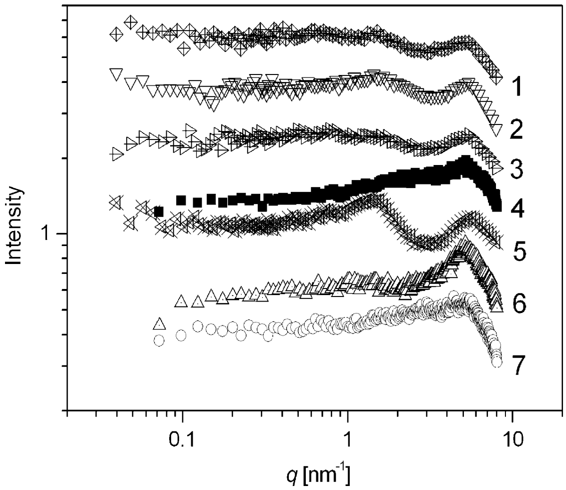

Fig. 8. SAXS profiles of the hybrid networks for $r=1.5$. Curves: 1, oligomer 6; 2, oligomer 3; 3, oligomer 11; 4, oligomer 8; 5, oligomer 10; 6, oligomer 9; 7, oligomer 7. Curves are vertically shifted.

SSQO clusters as a core from which organic chains extend and separate the SSQO clusters.

Generally, a high and narrow interference maximum reveals a well ordered structure. The regularity of arrangement in the studied hybrid polymers depends on the length of oligomer chain and location of functional groups. The intermolecular interference maximum in Fig. 7 is slightly more distinct with the oligomers of the high molecular weight, implying that the ordering increases with increasing molecular weight of the oligomer. As it was discussed above, the oligomers with high molecular weight values prefer formation of intramolecularly branched SSQO clusters. The formation of domains with compact SSQO structure leads to marked micro-phase separation and a better arranged micellar structure. Likewise, it turns out that the oligomers with alkoxysilyl groups at the end of chain tend to form more regularly organized structures than those of the oligomers with functional groups in the middle of chain.

The distance between the SSQO clusters of micellar structure is determined by the length of 'pendant' oligomer chain [19,20]. From Fig. 7 it is obvious that the interference maximum is shifted to lower q values with increasing molecular weight. The determined values of correlation distances d are given in Table 1, where a correlation between molecular weight and d can be seen. In the reactions with stoichiometric amounts of water, the correlation distance increases with increasing molecular weight in the series 6–5–4 and 3–2–1 from 4.2 to 7.9 nm and from 3.7 to 5.7 nm, respectively. The oligomers with TMSPMA units at terminal positions ($T_2D_xI_y$) exhibit greater values of correlation distances than the oligomers with the TMSPMA units in the middle ($D_xT_2I_y$). In the former case, the whole oligomer is pendant on the SSQO cluster, while in the latter case, two parts of the chain are pendant, and the separation distance between SSQO clusters is smaller.

The ordered arrangement is disturbed in cross-linked oligomers as obvious in Fig. 8. The networks from oligomers 3 (curve 2) and 6 (curve 1) exhibit only indistinct maxima at lower q. Surprising is the absence of maximum or the presence of very indistinct maximum at low q values in the cases of bistrialkoxysilane oligomers with functional groups at the end of chain (curves 6,7). Similar systems with poly(oxypropylene) chain exhibit ordered structures with marked interference maxima [21]. The random co-oligomer exhibits a small maximum (curve 4) because there exists no unambiguously predominating correlation distance. Nevertheless, this maximum is shifted to greater angles, which means substantially shorter distances. The increase in functionality of studied oligomers (curve 5,6) probably leads to the formation of large SSQO clusters. The SAXS profile of oligomer 11 (curve 3) reveals very wide distribution of correlation distances caused by disordered structure. In the oligomer 10, unlike oligomer 11, only 4 TMSPMA units shows up more distinct maximum at low q values (curve 5), because of more regularly ordered structure.

3.7. Glass transition temperature

The structure of oligomers affects the polymerization course and properties of cross-linked products. Table 1 gives the glass transition temperature values, T_g, of the hybrid networks, determined by means of DDSC. As expected, the T_g values increase with increasing functionality of oligomer, and the highest value ($T_g=79$ °C) is observed with the oligomer having 6 cross-linking TMSPMA units, oligomer 11. Besides the high network density it must be taken into account that the hard SSQO structure immobilizes the organic chains, and this effect increases with increasing content of SSQO domains. On the other hand, the lowest value ($T_g=48$ °C) was found in the case of network based on the oligomer 3. In this system, having functional groups in the middle of chain, there occur numerous ring closure reactions, and the oligomer undergoes gelation very slowly (Table 1), which results in a polymer network with low cross-linking density and low T_g. The network from oligomer with the similar molecular weight and content of the Si-monomer, oligomer 6, exhibits a T_g value higher by 14 °C because the system contains a lower number of cycles, and the network density is higher.

4. Conclusions

The GTP technique was adopted to prepare eleven types of linear methacrylate co-oligomers containing three types of co-monomers-TMSPMA, DMAEMA and IBMA. The structure of oligomers was varied from the standpoints of molecular weight and of location of the monomers along the chain. Thanks to the presence of trimethoxysilyl groups, these oligomers can react with water via the so-called sol–gel process. The sol–gel process results in producing O–I hybrids with SSQO structures. The development of the SSQO structures depends on the competition between intermolecular condensation and cyclization. The SEC analysis of intermediates in the sol–gel processes indicates that relatively stable cyclic macromonomers are formed in the early reaction stage. The main structural parameter controlling the behavior of oligomer during sol–gel process is the position and number of monomers having trimethoxysilyl group in their chain, and the chain length. The increasing length of a chain and position of the functional groups in the middle of the chain lead to increased tendency to form cyclic SSQO structures. The oligomers, $D_{10.1}T_{2.0}I_{8.1}$, $D_{6.7}T_{2.0}I_{5.3}$, $T_{2.0}D_{10.1}I_{8.1}$, $T_2.0D_{6.7}I_{5.3}$, form micellar structures with SSQO nucleus and 'pendant' organic chains, and the systems do not gel. Below the limit of critical molecular weight ($D_{3.4}T_{2.0}I_{2.7}$, $T_{2.0}D_{3.4}I_{2.7}$) and with different arrangement of functional monomer in oligomer chain, i.e. the random arrangement (${}_{rd}T_{2.0}D_{10.1}I_{8.0}$), or the blocks at both ends of chain ($T_{1.0}D_{9.8}I_{7.9}T_{1.0}$), or increased functionality ($D_{10.2}T_{4.0}I_{6.1}$, $D_{10.1}T_{6.0}I_{4.1}$), the intermolecular condensation reactions become more significant. The cyclic macro-monomers formed in the early stage further react and finally the network is formed.

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References

[1] Kickelbick G. Prog Polym Sci 2003;28:83–114.
[2] Brinker CJ, Scherer GW. Sol–gel science. San Diego: Academic Press; 1990.
[3] Baney RH, Itoh M, Sakakibara A, Suzuki T. Chem Rev 1995;95:1409–30.
[4] Devreux F, Boilot JP, Chaput F, Lecomte A. Phys Rev 1990;A41:6901–9.
[5] Ng LV, Thompson P, Sanchez J, Macosko CW, McCormick AV. Macromolecules 1995;28:6471–6.
[6] Himmel B, Gerber T, Burger H. J Non-Cryst Solids 1990;1:119.
[7] Brunet F, Cabane B. J Non-Cryst Solids 1993;163:211.
[8] Fasce DP, Williams RJJ, Méchin F, Pascault JP, Llauro MF, Pétlaud R. Macromolecules 1999;32:4757–63.
[9] Loy DA, Baugher BM, Baugher CR, Schneider DA, Rahimian K. Chem Mater 2000;12:3624–32.
[10] Matějka L, Dukh O, Hlavatá D, Meissner B, Brus J. Macromolecules 2001;34:6904–14.
[11] Kelts LW, Armstrong NJ. J Mater Res 1989;4:423.
[12] Loy DA, Carpenter JP, Alam TM, Shaltout R, Dorhout PK, Greaves J, et al. J Am Chem Soc 1999;121:5413–25.
[13] Matějka L, Dukh O, Brus J, Simonsick WJ, Meissner B. J Non-Cryst Solids 2000;270:34–47.
[14] Sogah DY, Hertler WR, Webster OW, Cohen GM. Macromolecules 1987; 20:1473–88.
[15] Stockmayer WH. J Polym Sci 1952;9:69.
[16] Jeon HK, Macosko CW, Moon B, Haye TR, Yin Z. Macromolecules 2004;37:2563.
[17] Eisenberg P, Erra-Balsells R, Ishikawa I, Lucas JC, Mauri AN, Nonami H, et al. Macromolecules 2000;33:1940–7.
[18] Matějka L, Dukh O, Meissner B, Hlavatá D, Brus J, Strachota A. Macromolecules 2003;36:7977–85.
[19] Surivet F, Lam TM, Pascault JP, Mai C. Macromolecules 1992;25: 5742–51.
[20] Rodrigues DE, Brennan AB, Betrabet C, Wang B, Wilkes GL. Chem Mater 1992;4:1437–46.
[21] Matějka L, Dukh O, Kamišová H, Hlavatá D, Špírková M, Brus J. Polymer 2004;45:3267–76.