

Polyacrylate Effects on Tetraethoxysilane Polycondensation

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The ²⁹Si NMR spectroscopy was employed in the assessment of polyacrylate effects on the course of acid-catalyzed polycondensation of tetraethoxysilane. The DEPT pulse sequence was used to achieve the sensitivity enhancement required for obtaining qualitatively and quantitatively interpreted ²⁹Si NMR spectra. Assessment of changes in concentration of reaction products during polycondensation and comparison of mole distribution of chain molecules of reaction systems, which contain different amounts of polyacrylate, has shown that polyacrylate affects polycondensation reactions considerably. The presence of polyacrylate slows up hydrolysis and condensation reactions significantly, and it enhances formation of cyclic products. By this method oligomer distribution changes in the reaction system significantly and the degree of condensation in siloxane gel increases. It is clear that polyacrylate does not act as a single filler, but it changes a structure of siloxane network as well.

Introduction

To achieve suitable properties of the resulting product, organic monomers or polymers can be introduced into the siloxane network formed by alkoxy silane polycondensation. For these purposes various types of polymers were used, e.g., poly(dimethylsiloxane),^{1,2} polyimides,³ or polyacrylates.⁴ Some polymers can be bounded chemically into a siloxane network due to a presence of hydrolyzable groups.⁵ A new type of inorganic-organic hybrid materials based on combinations of alkoxy silanes and polyacrylates formed by sol-gel processes finds application also in preserving processes, as agents for stone reinforcing.^{6–12} The copolymer of methylacrylate and ethyl methacrylate is the most widely used polyacrylate for these purposes (Paraloid B 72, Rohm & Hass). Out of the alkoxy silanes, tetraethoxysilane (TEOS), methyltriethoxysilane (MTEOS), and methyltrimethoxysilane (MTMOS) are used.

Despite the fact that these materials are used quite frequently, the mechanism of hybrid inorganic-organic gel formation has not been described sufficiently so far.

The data in the literature^{6,13,14} suggest that the nature, appearance, and structure of the resulting solid products strongly depend on the general composition of the reaction mixture and on the type of alkoxy silane and catalyst employed for polycondensation. Transparent, glasslike products can be obtained only by acid-catalyzed polycondensation of a mixture of TEOS with polyacrylate,^{6,13} and it is obvious that polyacrylates containing hydrolyzable alkoxy silane functional groups, which allow covalent bonding between the organic polymer chains and the silica matrix, provide single-phase materials.⁵ If basic catalyst was employed, e.g., morpholine,¹³ or polycondensation of MTMOS and polyacrylate mixture were not catalyzed at all, the resulting products have a nonhomogeneous structure and are opaque.^{6,14} When the structure of these products was studied in detail,^{6,14} it was found that nonhomogeneous material includes spherical-shaped silica particles, having a diameter of 15–100 μm , while polyacrylate is to be found in the space between these particles. Mechanical qualities of such a material are impaired considerably. Moreover, it was discovered that the presence of polyacrylate increased the degree of condensation and cross-linking of a siloxane network. Reasons for this situation were explained by the fact that after the gelation point of mixture, polyacrylate supported alkoxy silane polycondensation.⁶

Presently we can see an effort for the generation of hybrid inorganic-organic materials having the suitable properties. These materials were named as CERAM-ERs or ORMO-ERs (organically modified ceramics).¹⁵ Despite the fact that many studies were devoted to alkoxy silane polycondensation,^{16–26} the effects of acrylate polymer to TEOS polycondensation has not been

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Table 1. Composition of Reaction Mixtures (Contents of Low Molecular Reaction Components Expressed by Molar Ratio and Contents of Polyacrylate Expressed in Weight Percentage *w*)

no.	η (20 °C) [mPa s]	molar ratio				<i>w</i> (polyacrylate) [wt %]
		TEOS/ H ₂ O	TEOS/ HCl ^b	TEOS/ C ₂ H ₅ OH ^c	TEOS/ C ₄ H ₈ O ₂ ^d	
1	1.35	1/1	1/0.03	1/1.55	1/1.11	0
2	1.73	1/1	1/0.03	1/1.55	1/1.09	1 ^e
3	3.31	1/1	1/0.03	1/1.55	1/0.81	4 ^e
4	1.55	1/1	1/0.03	1/1.55	1/1.09	1 ^f
5	2.23	1/1	1/0.03	1/1.55	1/0.81	4 ^f

^a TEOS, tetraethoxysilane, 99.8 wt %, Synthesia Kolín, Czech Rep. ^b HCl, hydrochloric acid, 35.0 wt % p.a., Lachema Brno, Czech Rep. ^c C₂H₅OH, ethanol 99.8 wt % p.a., Merck, Germany. ^d C₄H₈O₂, dioxane, 99.8% p.a., Lachema Brno, Czech Rep. ^e Copolymer of ethyl methacrylate (70 mol %) and methylacrylate (30 mol %). Weight-average molecular weight 66.6 × 10³. Number-average molecular weight 29.7 × 10³ (produced by Rohm & Hass, Philadelphia). ^f Copolymer of methyl methacrylate (50%) and butyl acrylate (50%). Weight-average molecular weight 30.9 × 10³. Number-average molecular weight 7.9 × 10³ (produced by VUSPL Pardubice, Czech Rep.).

described sufficiently. It has been observed that during polycondensation of TEOS and poly(dimethylsiloxane) (PDMS), the self-condensation reaction of TEOS was predominant rather than copolymerization between PDMS and TEOS. As the reaction time increased, copolymerization between TEOS and PDMS was promoted. Furthermore it was found, that PDMS chains was broken into shorter chains under acid condition and with increasing temperature copolymerization between TEOS and PDMS became more extensive.² During polycondensation TEOS and *N*-[3-(triethoxysilyl)propyl]-2,4-dinitrophenylamine (TDP) a small extent of copolymerization was observed. The copolymerization proceeds in such a way that cross-linking occurred only among the TEOS-derived species and the TDP derived species remained as linear units.²⁷

In our work we studied the effects of polyacrylate on the course of acid-catalyzed polycondensation of TEOS. Our aim was to specify the effects of polyacrylate on the kinetics and on the mechanism of formation of the products of TEOS polycondensation during the initial phases of the sol-gel process. To study TEOS polycondensation, ²⁹Si NMR spectrometry was employed.

Experimental Section

Composition of Reaction Mixtures. To assess the effects of polyacrylate on the polycondensation course, five reaction mixtures were prepared, which contained different amounts and types of polymer. The exact composition of reaction mixtures is given in Table 1. Each of these mixtures contained

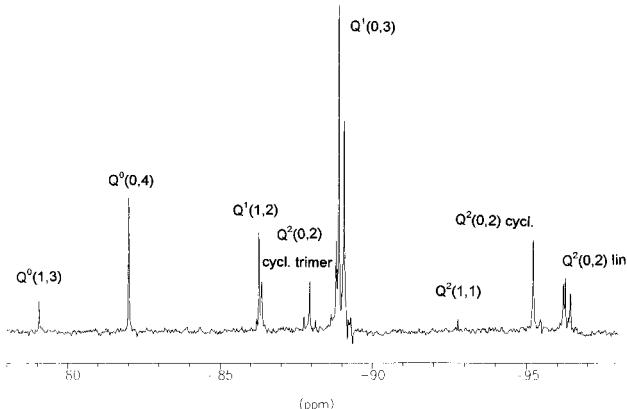


Figure 1. ²⁹Si NMR spectrum of the reaction mixture no. 2 (1 wt % of polyacrylate) obtained after 180 min by using DEPT sequence with transfer time 142 ms and θ pulse angle 24°. Relaxation delay 10 s, number of transitions 32. The values of chemical shift are given in ppm relative to TMS.

0.5 mL of deuterium dioxane-*d*₈ (Merck, 99.5% D), which is needed for field stabilization during the measurement of NMR spectra. The final pH value of the mixture is 1.0, and the concentration of TEOS was always 2.03 mol dm⁻³. The total volume of the mixture is 3.8 mL. The application of an ethanol-dioxane mixed solvent was necessary to obtain a perfect mixture and sufficient level of homogenization of all components of the reaction mixture.

Parameters of NMR Experiments. ²⁹Si NMR spectra of mixtures were obtained at 75.9 MHz on Bruker AM 400 spectrometer with a 10 mm broad-band probe with an internal deuterium stabilization. The DEPT pulse sequence was used for the sensitivity enhancement.^{20-22,24,28-30}

Experimental conditions: number of data point 32K, variable pulse angle $\theta = 24^\circ$, transfer time $\tau = 142$ ms, number of scans 32, temperature 303 K, and recycle delay 10 s.

Results and Discussion

The ²⁹Si NMR spectra were evaluated in both quality and quantity. The typical ²⁹Si NMR spectrum is given in Figure 1. In description of ²⁹Si NMR spectra, the Q^{*n*(*i,j*) notation was used, where Q indicates a four-function structural unit and *i*, *j*, and *n* respectively correspond to the number of -OH, -OC₂H₅, and siloxane functional groups bonded on the silicon atom. The main groups of resonance were easily assigned according to their chemical shift. The fact that many signals were described by the same symbols results from the situation where the chemical shift of Si atom does not depend only on the number of -OH, -OC₂H₅, and -OSi≡ groups bonded to the Si atom, but it is also affected by the length, size, and shape of the molecule in which the Si atom is situated.^{20-22,24} Interpretation of ²⁹Si NMR spectra is based on data given in the literature,^{19-21,24} and chemical shifts of individual Si species are listed in Table 2.}

Quantitative evaluation of polycondensation course is based on the values of integral intensity of signals, which had been corrected according to

$$E_d = m[\gamma(^1H)I\gamma(^{29}Si)] \times \sin \theta \cos^{m-1} \theta \sin(^3J_{H, Si}\pi\tau) \cos(^3J_{H, H}\pi\tau) \quad (1)$$

Equation 1 describes the relative intensity enhancement

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Table 2. Chemical Shifts of Species $Q^n(i,j)$ in the TEOS/C₂H₅OH/C₄H₈O₂/H₂O Mixture (Values Given in ppm with Respect to TMS)

δ (ppm)	species $Q^n(i,j)$	structural unit ^a
-79.05	$Q^0(1,3)$ monomer	$\text{HO}-\text{Si}^*-(\text{OEt})_3$
-82.02	$Q^0(0,4)$ monomer	$\text{Si}^*-(\text{OEt})_4$
-86.27	$Q^1(1,2)$ dimer	$\text{HO}-\text{Si}^*(\text{OEt})_2-\text{O}-\text{Si}(\text{OEt})_3$
-86.36	$Q^1(1,2)$ higher linear	$\text{HO}-\text{Si}^*(\text{OEt})_2-\text{O}-[\text{Si}(\text{OEt})_2]_n-\text{O}-\text{Si}-(\text{OEt})_3^c$
-87.95	$Q^2(0,2)$ cycl trimer	$-\text{[Si}^*(\text{OEt})_2-\text{O}]_3-$
-88.90	$Q^1(0,3)$ dimer	$\text{Si}^*(\text{OEt})_3-\text{O}-\text{Si}^*(\text{OEt})_3$
-88.81	$Q^1(0,3)$ dimer	$\text{HO}-\text{Si}(\text{OEt})_2-\text{O}-\text{Si}^*(\text{OEt})_3$
-89.07	$Q^1(0,3)$ higher linear	$\text{Si}^*(\text{OEt})_3-\text{[O}-\text{Si}(\text{OEt})_2]_n-\text{O}-\text{Si}^*(\text{OEt})_3^c$
-92.78	$Q^2(1,1)$ lin trimer	$\text{Si}(\text{OEt})_3-\text{O}-\text{Si}^*(\text{OH})(\text{OEt})-\text{O}-\text{Si}-(\text{OEt})_3$
-95.21	$Q^2(0,2)$ cycl tetramer	$-\text{[Si}^*(\text{OEt})_2-\text{O}]_4-$
-95.45	$Q^2(0,2)$ cycl pentamer	$-\text{[Si}^*(\text{OEt})_2-\text{O}]_5-$
-96.19	$Q^2(0,2)$ lin trimer	$\text{HO}-\text{Si}(\text{OEt})_2-\text{O}-\text{Si}^*(\text{OEt})_2-\text{O}-\text{Si}-(\text{OEt})_3$
-96.26	$Q^2(0,2)$ lin trimer	$\text{Si}(\text{OEt})_3-\text{O}-\text{Si}^*(\text{OEt})_2-\text{O}-\text{Si}-(\text{OEt})_3$
-96.35	1st $Q^2(0,2)$ in linear chains ^b	$\text{Si}(\text{OEt})_3-\text{O}-\text{Si}^*(\text{OEt})_2-\text{[O}-\text{Si}(\text{OEt})_2]_n-\text{O}-\text{Si}(\text{OEt})_3^c$
-96.43	2nd $Q^2(0,2)$ in linear chains ^b	$\text{Si}(\text{OEt})_3-\text{O}-\text{Si}(\text{OEt})_2-\text{O}-\text{Si}^*(\text{OEt})_2-\text{[O}-\text{Si}(\text{OEt})_2]_n-\text{O}-\text{Si}(\text{OEt})_3^c$

^a Si^* : observed ^{29}Si . ^b Meant symmetrically from both ends of the chains. ^c $n \geq 1$.

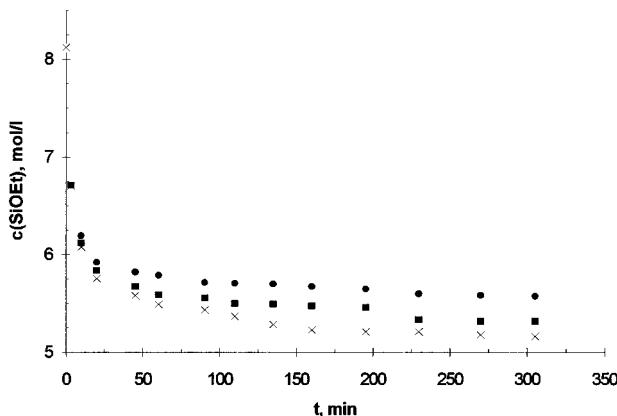


Figure 2. Time dependence of concentration of $\equiv\text{SiOEt}$ groups. (x) mixture no. 1, (■) mixture no. 2, (●) mixture no. 3.

E_d of signals of ^{29}Si atoms, in which m is number of ^1H atoms coupled to ^{29}Si , $\gamma(^1\text{H})$ and $\gamma(^{29}\text{Si})$ are the values of gyromagnetic ratio, θ is a variable pulse angle, $^3J_{\text{H},\text{Si}}$ is the coupling constant $^1\text{H}-^{29}\text{Si}$, $^3J_{\text{H},\text{H}}$ is coupling constant $^1\text{H}-^1\text{H}$, and τ is the polarization transfer time.^{21,26} Further on the results obtained were put into diagrams as time dependencies of relative concentration of $Q^n(i,j)$ species and concentration of $\equiv\text{SiOH}$ and $\equiv\text{SiOC}_2\text{H}_5$ groups. The effects of the presence of polyacrylate on the rate of formation and quantity of individual species $Q^n(i,j)$ as well as on the rate of formation and quantity of individual products of TEOS polycondensation were demonstrated on these dependencies.

In the first part of the evaluation of experimental results we studied the effects of polyacrylate on TEOS polycondensation kinetics. Overall information about the course of hydrolysis and condensation of individual reaction mixtures provide time dependencies of concentration of $\equiv\text{SiOC}_2\text{H}_5$ and $\equiv\text{SiOH}$ groups, which are shown in Figures 2 and 3. These time dependencies are shown only for mixtures 1–3, because the second two time dependencies for mixtures 4 and 5 are very similar. As it results from these dependencies, the effects of polyacrylate vary in time considerably. We suppose that in the initial phase of hydrolysis, when the mixture contains a relatively high amount of water, the effect of the presence of polyacrylate is negligible and cannot be followed up by the method employed. This conclusion results from a comparison of changes in the concentration of $\equiv\text{SiOC}_2\text{H}_5$ groups during the first 5–10 min of

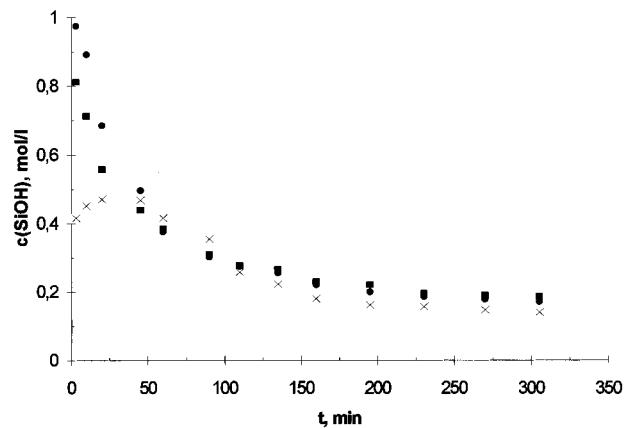


Figure 3. Time dependence of concentration of $\equiv\text{SiOH}$ groups. (x) mixture no. 1, (■) mixture no. 2, (●) mixture no. 3.

polycondensation, in which the course of time dependencies is almost identical in all cases (cf. Figure 2). However, a considerably increased concentration of $\equiv\text{SiOH}$ groups in mixtures containing polyacrylate (cf. Figure 3) can be seen during this time interval. As the initial decrease of the concentration of $\equiv\text{SiOC}_2\text{H}_5$ groups was identical in all cases, it seems that polyacrylate macromolecules prevent subsequent condensation of existing hydrolysis products (silanol)s, which are accumulated in the mixture temporarily. Intensive slowing effect of polyacrylate on the TEOS hydrolysis occurs in later phases of the reaction. It can be documented by a relatively rapid decrease of $\equiv\text{SiOH}$ groups in the mixtures containing polyacrylate. The most intensive decrease of concentration of $\equiv\text{SiOH}$ groups occurred in the mixture with higher viscosity containing the highest amount of polyacrylate with higher molecular weight.

We can suppose that the presence of polyacrylate prevents both hydrolysis of alkoxy groups and the following condensation of silanol groups. At the beginning of the reaction we cannot observe the slowing of the hydrolysis because of the relatively high amount of water. By hydrolysis retardation, if compared with the initial phase, a relatively high decrease of the concentration of $\equiv\text{SiOH}$ groups can be explained in the mixtures containing polyacrylate. The formation of new $\equiv\text{SiOH}$ groups is suppressed, while amount of existing hydroxyl groups is reduced continuously during the condensation reaction. At the same time the condensation reactions are retarded, and that is why the total concentration of $\equiv\text{SiOH}$ groups in the mixture contain-

Table 3. Momentary Values of the Alcohol-Producing Condensation Rate Constants k_{ca} Calculated for Reaction Mixture Nos. 1–5

no.	time [min]										
	20	45	60	90	110	135	160	195	230	270	305
1	3.00	2.18	2.00	1.51	1.41	1.31	1.22	1.03	0.87	0.78	0.71
2 $k_{ca}/10^{-3}$	2.24	1.74	1.40	1.15	1.07	0.90	0.86	0.67	0.71	0.62	0.55
3 [$\text{dm}^3 \text{mol}^{-1} \text{min}^{-1}$]	1.80	1.06	0.90	0.76	0.65	0.54	0.49	0.42	0.41	0.36	0.33
4	2.25	1.80	1.51	1.20	1.15	0.94	0.90	0.75	0.70	0.65	0.60
5	1.95	1.30	1.15	0.97	0.85	0.70	0.65	0.50	0.59	0.48	0.41

Table 4. Momentary Values of the Water-Producing Condensation Rate Constants k_{cw} Calculated for Reaction Mixture Nos. 1–5

no.	time [min]										
	20	45	60	90	110	135	160	195	230	270	305
1	18.0	4.50	3.50	3.40	3.10	2.85	2.50	2.41	2.50	2.35	2.24
2 $k_{cw}/10^{-3}$	17.0	3.62	3.28	2.71	2.31	2.30	2.10	1.85	1.59	1.23	1.34
3 [$\text{dm}^3 \text{mol}^{-1} \text{min}^{-1}$]	16.0	6.05	4.09	2.85	2.13	1.80	1.80	1.75	1.35	0.95	0.80
4	17.0	3.71	3.35	2.87	2.61	2.52	2.26	1.98	1.75	1.48	1.37
5	16.0	5.00	3.89	2.75	2.26	2.15	2.02	1.76	1.49	1.22	1.12

ing polyacrylate is higher than that in a mixture without polyacrylate. We can conclude that polyacrylate exhibits retarding effects on both hydrolysis and polycondensation, while retardation of hydrolysis becomes significant at the moment when water content in the mixture was reduced.

As for quantitative evaluation, the retarding effect of polyacrylate on polycondensation of silanol groups can be assessed by a comparison of the rate constants of condensation reactions. These rate constants can be calculated by the following kinetic equations:

$$\frac{d[\text{SiOR}]}{dt} = -k_h[\text{SiOR}][\text{H}_2\text{O}] - \frac{1}{2}k_{ca}[\text{SiOH}][\text{SiOR}] \quad (2)$$

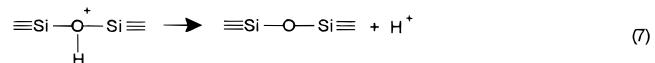
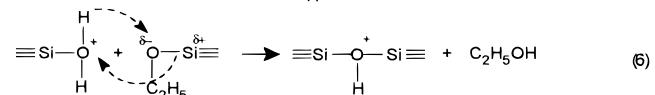
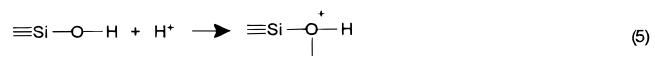
$$\frac{d[\text{SiOH}]}{dt} = k_h[\text{SiOR}][\text{H}_2\text{O}] - \frac{1}{2}k_{ca}[\text{SiOH}][\text{SiOR}] - k_{cw}[\text{SiOH}]^2 \quad (3)$$

$$\frac{d[\text{SiOSi}]}{dt} = k_{cw}[\text{SiOH}]^2 + k_{ca}[\text{SiOH}][\text{SiOR}] \quad (4)$$

on the condition that the reactivity of hydroxyl and ethoxyl groups is the constant during the polycondensation, and hydrolysis and condensation, in which water as well as ethanol are released, occur in the course of the sol–gel process.^{21–23} Then k_h is the hydrolysis rate constant, k_{ca} is the alcohol-producing condensation rate constant, and k_{cw} is the water-producing condensation rate constant. Methods of rate constant calculations and detailed description of kinetic model are given in refs 21–23.

As there are not sufficient data for calculation of the hydrolysis rate constant, the value given here should be considered approximate. A k_h hydrolysis rate constant was calculated for all five reaction mixtures, and it is approximately $k_h > 0.13 \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$. When condensation rate constants were calculated, the great deflection from the theoretical assumption saying that the reactivity of all polycondensation products is constant during the entire process became evident. As given in Tables 3 and 4, momentary values of rate constants k_{ca} and k_{cw} decrease during polycondensation and that fact is closely related to inductive and steric effects. At very low pH values (below isoelectric point, $\text{pH} < 2.0$) an electrophilic mechanism is supposed in both hydrolysis and condensation. Under these conditions silanol groups are protonated²³ and we can suppose that the oxide atom of the hydroxyl group acts as

a reaction center. A mechanism of condensation, in which ethanol is released, can be described by



As a negative inductive effect of function groups decreases in the series $-\text{I}(-\text{OH}) > -\text{I}(-\text{OC}_2\text{H}_5) > -\text{I}(-\text{O}—\text{Si} \equiv)$, it is obvious that the substitution of $\text{C}_2\text{H}_5\text{O}^-$ by a hydroxyl group leads to an increase in the density of positive charge in the Si atom and by way also to an increase of negative charge in oxide atom, which is then more susceptible to electrophilic condensation. On the other hand, substitution of $\text{C}_2\text{H}_5\text{O}^-$ or $-\text{OH}$ groups by siloxane leads to a decrease in the density of the positive charge in the Si atom and to a decrease of negative charge in oxide atom. The result is that this atom is less susceptible to electrophilic attack. It results from the above given facts that reactivity of species decreases in the series $\text{Q}^0 > \text{Q}^1 > \text{Q}^2$ and species containing OH^- groups are more reactive. From this reason it is not very useful to specify mean values of rate constants. However, from values listed in Tables 2 and 3 we can state that with increasing content of polyacrylate, with increasing of viscosity of solution, and with increasing of molecular weight of polyacrylate the values of condensation kinetic constant decrease.

To assess the general rate of polycondensation, it is better to compare the time dependencies of the degree of condensation in the individual reaction mixtures. The condensation degree p is defined¹⁷ by

$$p = \sum_n n q_n / f \quad (8)$$

where q_n is the relative concentration of species Q^n , n is the number of siloxane bonds available in the given structural unit, and f is the connectivity of the monomer ($f = 4$ for TEOS). It results from a comparison of these dependencies (cf. Figure 4) and from values of $dp/d \log t$ (0.122, 0.107, 0.095, 0.115, and 0.101 for reaction

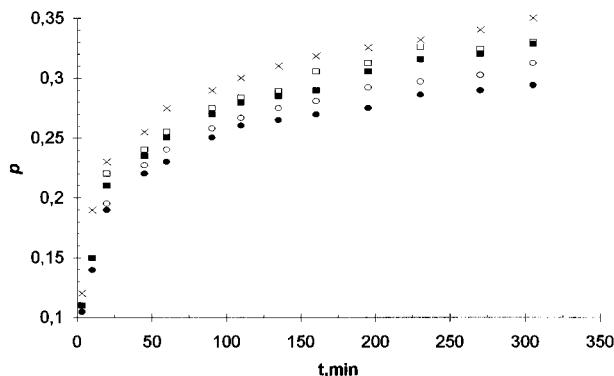


Figure 4. Time dependence of degree of condensation p . (×) mixture no. 1, (■) mixture no. 2, (●) mixture no. 3, (□) mixture no. 4, (○) mixture no. 5.

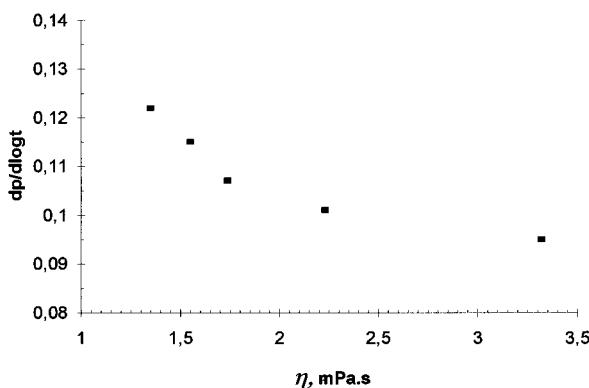


Figure 5. Dependence of $dp/d \log t$ on viscosity of solution at the constant degree of condensation $p = 0.29$.

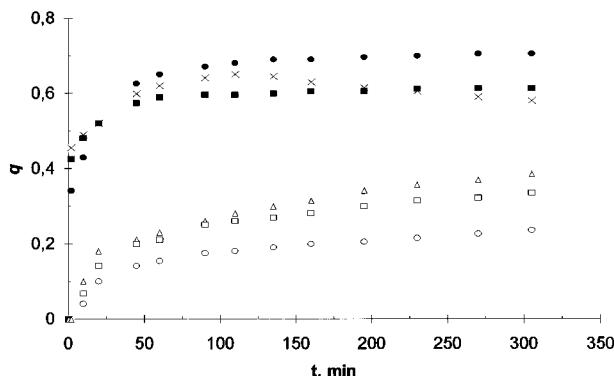


Figure 6. Time dependence of relative concentration q of species Q^1 (×) mixture no. 1, (■) mixture no. 2, (●) mixture no. 3 and Q^2 (△) mixture no. 1, (□) mixture no. 2, (○) mixture no. 3.

mixtures 1–5, respectively) that the total rate of polycondensation decreases with increasing polyacrylate content, viscosity of solution, and molecular weight of polymer. This retardation is caused by the presence of large polyacrylate molecules in the mixture, which limit the mobility of siloxane molecules (cf. Figure 5).

The presence of polyacrylate in the reaction mixture affects not only the polycondensation rate but also the extent of reactions. As follows from Figure 6, the time dependence of the relative concentration of species Q^1 in the mixtures containing polyacrylate is constant after a certain time break point of reaction. This is probably caused by the fact that the mutual condensation of dimers and higher oligomers is suppressed in these mixtures and condensation preferably occurs among monomers and dimers or monomers and other oligomers, during which Q^1 species are not consumed. At

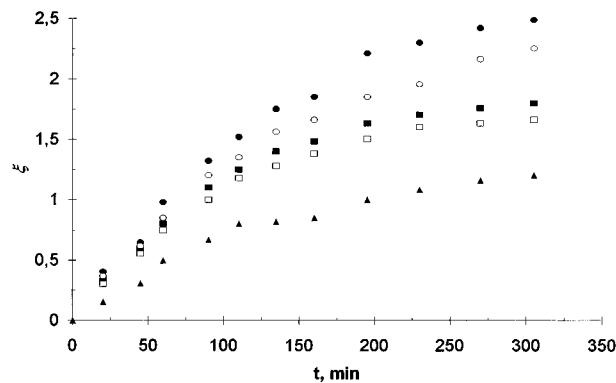


Figure 7. Time dependence of molar ratio ξ of Q^2 species contained in cyclic and linear products ($\xi = Q_{\text{cycl}}^2/Q_{\text{lin}}^2$): (×) mixture no. 1, (■) mixture no. 2, (●) mixture no. 3, (□) mixture no. 4, (○) mixture no. 5.

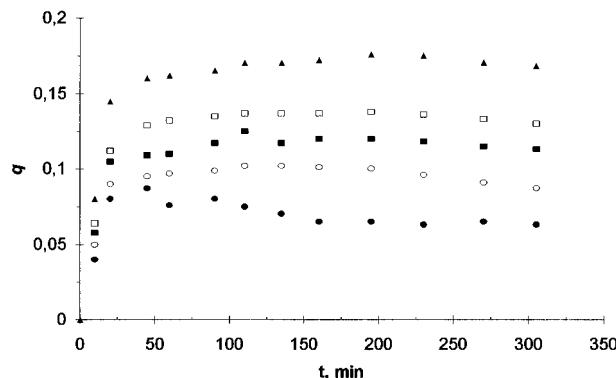


Figure 8. Time dependence of relative concentration q of species Q^2 contained in linear products: (×) mixture no. 1, (■) mixture no. 2, (●) mixture no. 3, (□) mixture no. 4, (○) mixture no. 5.

the same time the rate of dimer formation must correspond to the rate of cyclization reactions.

To assess the extent of cyclization reactions during the TEOS polycondensation, we have to follow up the content of ^{29}Si atoms of Q^2 type within in both linear and cyclic oligomers during the polycondensation process. The extent of cyclization, ξ , can be defined by a ratio of concentration of Q^2 species linked in cyclic and linear molecules according to

$$\xi = Q_{\text{cycl}}^2/Q_{\text{lin}}^2 \quad (9)$$

The time dependence of ξ is given in Figure 7.

It was shown that with increasing content of polyacrylate in the mixture, the extent of cyclization reactions increases, while the decrease of concentration of Q^2 species linked within linear molecules (cf. Figure 8) is given just by this cyclization, as formation of more condensed Q^3 species was not found. This phenomenon is directly associated with the mobility of the molecules, which undergo cyclization more easily in an environment where their mobility is limited. This reaction is more probable to occur, rather than mutual condensation resulting in prolongation of the linear chain. The higher extent of cyclization reactions explains the phenomenon, which was described in ref 6, which mentioned the situation in which a higher degree of condensation and cross-linking had been discovered in solid products, which had been generated by polycondensation of the alkoxy silane mixture in the presence of polyacrylate, if compared with the products having been generated without the presence of polymers.

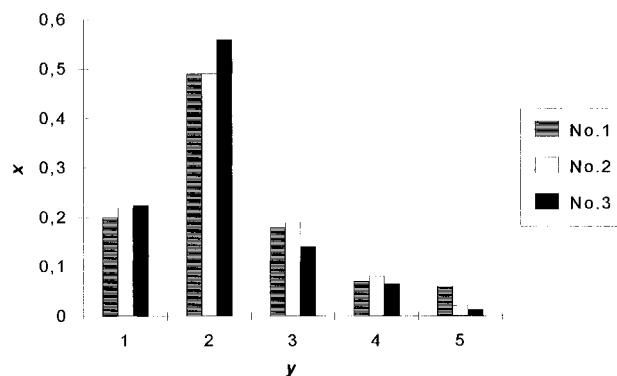


Figure 9. Comparison of mole fraction distributions of chain molecules for the reaction mixtures with the constant degree of condensation $p = 0.29$.

Polyacrylate effects on distribution of individual oligomers in the mixture can be assessed by determination of the mole fraction distribution of chain molecules. The mole fraction distribution of chain molecules has to be determined at the chosen constant degree of condensation. By this method time as parameter as well as differences in polycondensation rate can be eliminated. In our case we chose the highest possible degree of condensation that could be reached in reaction mixture no. 3, i.e., $p = 0.29$. It results from a comparison of the mole fraction distribution, shown in Figure 9, that the presence of polyacrylate reduces the content of pentamers in the mixture considerably. As follows from the mole ratio of cyclic and linear oligomers in the individual oligomer fractions (see Table 5), the low content of pentamers in the mixture is caused by cyclization of trimers and tetramers, resulting in a limitation of further chain prolongation. An absence of cyclic pentamers in mixture no. 3, containing the highest amount of polyacrylate with higher molecular weight can be explained by the fact that the mixture generally contains only a very low amount of linear pentamers, by cyclization of which cyclic pentamers are formed. Its quantity is then below the detection limit.

Higher range of cyclization reactions also affects number average of degree of polymerization, which was calculated from the given mole fraction distributions of chain molecules, according to

$$\bar{X}_n = \sum_i x_i y_i \quad (10)$$

where x_i is the mole fraction of oligomer having polymerization degree y_i . To keep a constant condensation degree in all five mixtures under reaction, a reduction of the average chain length resulting from values of \bar{X}_n (2.31, 2.19, 2.08, 2.25, and 2.15 for reaction mixtures 1–5, respectively) has to be compensated for by a relative increase of their cyclization, as the condensation degree increases during cyclization, without changing the chain length (cf. Figure 10).

Conclusion

It was proved by the experiments made that the presence of polyacrylate in the mixture affects both

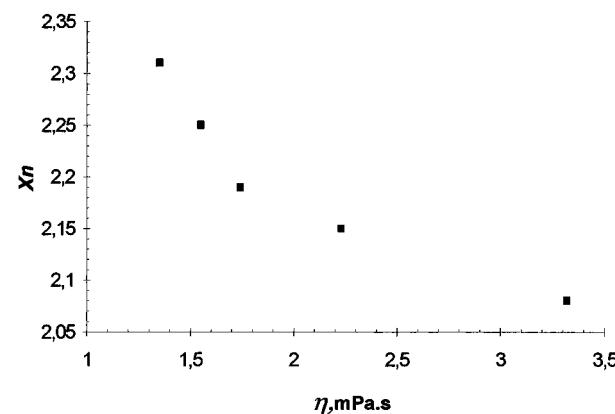


Figure 10. The dependence of number average of degree of polymerization \bar{X}_n on viscosity of solution at the constant degree of condensation $p = 0.29$.

Table 5. Molar Ratio of Cyclic and Linear Oligomers in Each Oligomer Fraction (Degree of Condensation of Reaction Mixture $p = 0.29$)

no.	trimer		tetramer		pentamer	
	cyclic	linear	cyclic	linear	cyclic	linear
1	0.12	0.88	0.54	0.46	0.16	0.84
2	0.18	0.82	0.65	0.35	0.26	0.74
3	0.47	0.53	0.71	0.29	0.0	1.00
4	0.16	0.84	0.61	0.39	0.20	0.80
5	0.27	0.73	0.68	0.32	0.30	0.70

Polycondensation kinetics and the abundance of individual oligomers in the reaction mixture. It is obvious that in the environment where polyacrylate macromolecules are present, the total polycondensation rate is reduced. In initial phases the polyacrylate effect on hydrolysis is very small, but later on, with decreasing water content in a mixture, it can be seen as a considerable reduction of its rate. The presence of polyacrylate in the mixture also affects the course of the condensation reaction considerably. Large polyacrylate macromolecules probably reduce the condensation rate, as they prevent mutual collisions between various siloxane molecules, in which their reaction takes place as well as prolongation of their chains. That is why intramolecular cyclization reactions are preferred to prolongation of linear chains. By this way, the presence of polyacrylate in the mixture can increase the degree of condensation and cross-linking of the network in a solid product. It is obvious that polyacrylate does not act only as an inert filler of siloxane gel, but it directly affects the structure of the siloxane network created. It is important that the above-described phenomena directly depend on viscosity of solutions.

Further on it was shown that steric and inductive effects under the given conditions affect the reactivity of the products resulting from hydrolysis and polycondensation. These effects are so intensive that a considerable decrease of momentary rate constants of condensation, k_{ca} and k_{cw} , does not make it possible to specify mean value or effective rate constants.