^{29}Si NMR STUDY OF DISTRIBUTION OF OLIGOMERS IN POLYCONDENSATION OF TETRAETHOXYSILANE

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^{29}Si NMR spectrometry has been used to determine the number molecular weight distribution of polymerization degrees of a system of oligomers formed in the sol–gel polycondensation of tetra-ethoxysilane (TEOS). On the basis of identification of the oligomers, monitoring of the concentration changes during the initial phase of the sol–gel polycondensation, and from the deviations observed between the experimentally determined number molecular weight distribution of polymerization degrees and the Flory–Stockmayer model it has been proved that cyclization represents a significant process in the acid-catalyzed polycondensation with substoichiometric amount of water (ratio of amounts TEOS/H_2O = 1 : 1). The cyclization becomes important at the moment when the reaction mixture contains increased amounts of the linear tetramer and pentamer. The cyclization products form a basis for formation of polycyclic, highly condensed building units whose gradual aggregation produces the gel.

Key words: Sol–gel; Polymerization degree, mole fraction distribution of; ^{29}Si NMR DEPT.

Polycondensation of alkoxysilanes, mostly tetraethoxysilane (TEOS) and methyl-triethoxysilane (MTEOS) is applied, inter alia, to stone consolidation in the techology of monument conservation. The initial phase of polycondensation is important for the character of the gel formed. In literature considerable space has been given to acid-catalyzed sol–gel polycondensation of alkoxysilane taking place with an overstoi-chiometric amount of water[1–5]. At such conditions a rapid and complete hydrolysis takes place at first. During the subsequent polycondensation, formation of small, highly condensed building units of 0.7 nm magnitude was observed: they contain 8–10 silicon atoms and their stepwise aggregation forms a gel[2]. The magnitude of these units at the point of gelation is about 5 nm and agrees well with the magnitude of the primary particles forming the solid gel (which varies from 3 to 6 nm); from the primary par-ticles the secondary particles of 10–30 nm magnitude are formed which can be proved by the electron microscopy[6,7]. The formation of cyclic structures was also confirmed[8] by X-ray diffraction on a gel of SiO_2 prepared by the polycondensation of MTEOS.

The content of water in reaction mixture is decisive for the hydrolysis degree and, hence, subsequently for the rate and degree of the polycondensation. It is, therefore, likely that it affects also the mechanism of formation of the gel and its final properties. There exist different opinions as to the extent of the cyclization reactions taking place during a polycondensation with substoichiometric amount of water in the reaction mixture, the prevailing one stating that decreasing water content in the reaction mixture decreases the proportion of cyclization reactions[1,10]. A comparison of the polycondensation kinetics of tetramethoxysilane (TMOS) in methanol with the statistical kinetic model also showed that the reactions do not correspond to a statistically random polycondensation but are affected by steric and/or inductive effects[9,10].

The aim of the present work was: to identify the individual polycondensation products by means of ^{29}Si NMR spectrometry and determine the number molecular weight distribution of polymerization degrees and the number average polymerization degree; to decide, on the basis of comparison of experimental data with theoretical prediction of the Flory–Stockmayer model[11], whether the cyclization is a significant process also in the acid-catalyzed polycondensation proceeding in the presence of low water content (TEOS/H$_2$O = 1 : 1) or rather linear chains are formed, which is just the case expected at the low water content[12,13].

EXPERIMENTAL

The reaction mixture (3.2 ml) was prepared by adding distilled water and hydrochloric acid (the water content 65.0% v/v) to a mixture of tetraethoxysilane (TEOS; Synthesia Kolin, Czech Republic), ethanol (distilled; water content 2.50% v/v), and 0.5 ml deuteriated ethanol (Merck; 99.6% D; water content 2.50% v/v). The molar ratios of components in reaction mixture: TEOS/H$_2$O = 1 : 1, TEOS/HCl = 1 : 0.03, TEOS/EtOH = 1 : 4.5. The TEOS concentration was 2.02 mol l^{-1}, the pH value of reaction mixture was 1.0.

The ^{29}Si NMR spectra of the mixture were measured in 10 mm closed glass cells using an FT NMR spectrometer Bruker AM 400 at the frequence of 75.9 MHz with internal deuterium stabilization and pulse sequence DEPT (refs[5,10,14–16]) to increase the selectivity: the number of scanned points 32 K, mixing pulse θ = 24°, the value of τ = 142 ms (which corresponds to J = 3.5 Hz, the coupling constant obtained by us for Si–O–C–H being J = 2.9 Hz), the number of accumulation FID was 32, temperature 303 K, the relaxation delay 10 s. The external standard HMDS was used for calibration of the ^{29}Si scale, the chemical shift of ^{29}Si having the value of 6 ppm referred to TMS.

RESULTS AND DISCUSSION

Application of ^{29}Si NMR spectrometry to a study of polycondensation of alkoxysilanes faces serious problems which complicate the experiment. The main problem lies in the low sensitivity of ^{29}Si nuclei given by the low negative gyromagnetic ratio (γ = –0.5412 . 10^8 rad T^{-1} s^{-1}) and low natural occurrence of the ^{29}Si isotope in nature (4.7%). In addition to that, the negative value of gyromagnetic ratio causes a negative nuclear Overhauser effect, which can result in a distinct decrease of intensity or complete disappearing of

signals. Hence, in order to obtain high-quality, quantitatively interpretable ^{29}Si NMR spectra one must distinctly increase the number of FID accumulations, which (with regard to the long relaxation times of [29]Si atoms) very much increases the time necessary for obtaining one spectrum. This is very inconvenient in the case of a dynamic system, and the data obtained are markedly distorted. However, these problems are avoided by using the DEPT pulse sequence[5,10,14–16] which makes use of the transfer of polarization from the adjacent hydrogen atom; moreover, then the ^{29}Si NMR spectra obtained do not show the broad silicon signal due to the glass of the cell.

In the range from –70 ppm to –120 ppm in the ^{29}Si NMR spectra we can observe a number of signals corresponding to a relatively high abundance of [29]Si in the hydrolyzed and condensed products. The formal designations of individual types of structurally bonded [29]Si atoms starts from the scheme $Q^s(h,r)$, where Q means the tetrafunctional structural units, s denotes the number of siloxane bonds, and h and r stand for the numbers of OH and OR groups, respectively, bound to the given Si atom.

Figure 1 presents a typical ^{29}Si NMR spectrum. The individual signals in the overview spectra were assigned to the basic types of structurally bound [29]Si atoms $Q^s(h,r)$. After expanding the regions of these signals it is possible to observe a number of further signals in them whose occurrence is due to the presence of structural units differing in magnitude and shape of the molecules in which these units are contained (Fig. 2). In this way it is possible to differentiate between the structurally bound [29]Si atoms having the same formal denotation but differing in their close neighbourhood and, hence, in their chemical shifts. It is possible to differentiate between the cyclic and linear polycondensation products and individual oligomers from dimer to hexamer[5,10]. For instance, the value of chemical shift of the structurally bound [29]Si atom $Q^1(0,3)$ lies in the interval from –88.80 ppm to –89.03 ppm, the chemical shift of signal of this atom
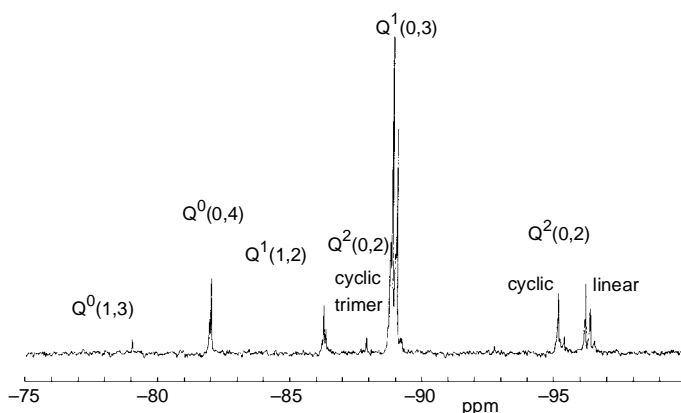

FIG. 1
Overview ^{29}Si NMR spectrum of the reaction mixture after 180 min

in the dimer (which has no OH group) having the value of –88.87 ppm. The value of chemical shift is also changed by lengthening of the molecule. Thus the chemical shift of structurally bound ^{29}Si atom of $Q^1(0,3)$ type in higher oligomers has the value of –89.03 ppm. The observed changes in values of chemical shifts of structural units of TEOS oligomers agree well with the literature data[5] which, however, concern the reaction mixtures starting from TMOS. Similar changes in values of chemical shifts can be observed also in the structurally bound ^{29}Si atoms $Q^2(0,2)$, on the basis of which it is possible to identify the individual oligomers (trimers, tetramers, and pentamers). First of all it is possible to differentiate between the structurally bound ^{29}Si atoms in cyclic and linear molecules. Generally it is true that the increasing density of positive charge at the silicon atom which induces paramagnetic shielding will cause a change in the chemical shifts toward more negative values. The signals of structurally bound ^{29}Si atoms of cyclic products of condensation – in contrast to the linear ones – show more positive values of chemical shift because the cyclization reduces the O–Si–O valence angles and, hence, the density of positive charge at silicon[2]. Particularly with the cyclic trimers is this reduction of valence angle distinct. Therefore the chemical shift of structurally bound ^{29}Si atom $Q^2(0,2)$ of cyclic trimer has a markedly more positive value than is the value of chemical shift of identically bound ^{29}Si atoms in the cyclic tetramer or pentamer. For similar reasons it is possible to differentiate between the structurally bound ^{29}Si atoms $Q^2(0,2)$ in various linear oligomers.

The interpretation of ^{29}Si NMR spectra measured is supported by literature data[1,2,4,5,18]; the assignment of the signals corresponding to individual oligomers in the expanded spectra made use (because of the lack of data on TEOS) of the analogy[5,10] concerning the oligomers formed by polycondensation of TMOS. The values obtained are summarized in Table I.
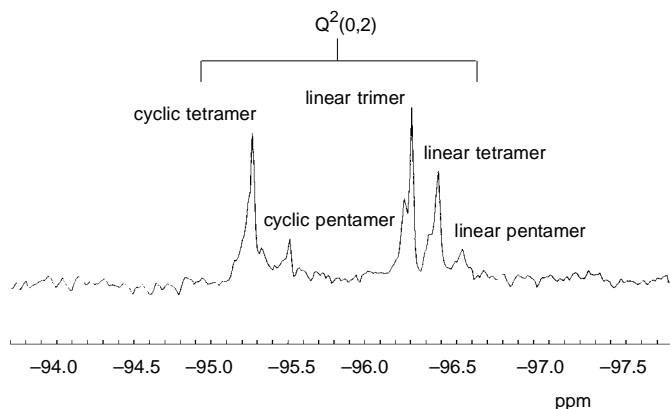

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Expanded part of ^{29}Si NMR spectrum from Fig. 1. The region shown corresponds to structurally bound ^{29}Si atoms of $Q^2(0,2)$ type

In this context it should be noted that the application of pulse sequence DEPT is restricted only to monitoring of the presence of such structurally bound silicon atoms which have at least one bond to ethoxyl group. Hence it is impossible to identify fully hydrolyzed products and a structurally bound [29]Si atom $Q^4(0,0)$. With respect to the low water content in the reaction mixture and relatively short time of monitoring of the polycondensation process, however, formation of such products is highly unlikely. This presumption is confirmed by the absence of the structural units containing more than one hydroxyl group and by the absence of more highly condensed structural units than Q^2 which can still be determined by this method. Hence the DEPT sequence used is only suitable for monitoring of the initial phase of the polycondensation with low water content.

At first, for quantitative evaluation of the polycondensation course, the relative intensities of signals, E_d, were standardized according to the equation

$$E_d = n[\gamma(^1H)/\gamma(^{29}Si)] \sin \theta \cos^{n-1} \theta \sin (\pi J \tau), \qquad (1)$$

TABLE I
Chemical shifts, δ, of signals of [29]Si in individual structural units against TMS ($\delta(^{29}Si)$ in TMS = 0 ppm)

δ, ppm	$Q^s(h,r)$	Structural unit with [29]Si atom[a]
−79.01	$Q^0(1,3)$	HO–**Si**–(OEt)$_3$
−82.01	$Q^0(0,4)$	**Si**–(OEt)$_4$
−86.27	$Q^1(1,2)$ dimer	HO–**Si**(OEt)$_2$–O–Si(OEt)$_3$
−86.37	$Q^1(1,2)$ higher linear polymer	HO–**Si**(OEt)$_2$–O–Si(OEt)$_2$–O–Si–
−87.91	$Q^2(0,2)$ cyclic trimer	–(**Si**(OEt)$_2$–O)$_3$–
−88.87	$Q^1(0,3)$ dimer	**Si**(OEt)$_3$–O–**Si**(OEt)$_3$
−88.80	$Q^1(0,3)$ dimer	HO–Si(OEt)$_2$–O–**Si**(OEt)$_3$
−89.03	$Q^1(0,3)$ higher linear polymer	**Si**(OEt)$_3$–O–Si(OEt)$_2$–O–Si–
−95.16	$Q^2(0,2)$ cyclic tetramer	–(**Si**(OEt)$_2$–O)$_4$–
−95.41	$Q^2(0,2)$ cyclic pentamer	–(**Si**(OEt)$_2$–O)$_5$–
−96.20	$Q^2(0,2)$ linear trimer	Si(OEt)$_3$–O–**Si**(OEt)$_2$–O–Si–(OEt)$_3$
−96.38	$Q^2(0,2)$ linear tetramer	Si(OEt)$_3$–O–(**Si**(OEt)$_2$)$_2$–O–Si–(OEt)$_3$
−96.53	$Q^2(0,2)$ linear pentamer	[Si(OEt)$_3$–O–Si(OEt)$_2$]$_2$**Si**(OEt)$_2$

[a] The structurally bound [29]Si atom is printed in bold letters.

in which n is the number of ^{1}H atoms at the adjacent carbon atom, $\gamma(^1H)$ and $\gamma(^{29}Si)$ are values of the respective gyromagnetic ratio, θ is the variable pulse angle, J is the coupling constant ^1H–^{29}Si and τ is the time of polarization transfer. Then the calculated values were treated graphically as time dependences of mole fraction of the structural units $Q^s(h,r)$ and are presented in Figs 3–6.

Basic information on behaviour of the system can be obtained by comparing the experimentally found values of mole fraction of the bound ^{29}Si atoms Q^s with the kinetic model whose detailed description can be found in refs[9,10,17]. This model starts from the presumption that the whole sol–gel process can be described by the kinetic equations
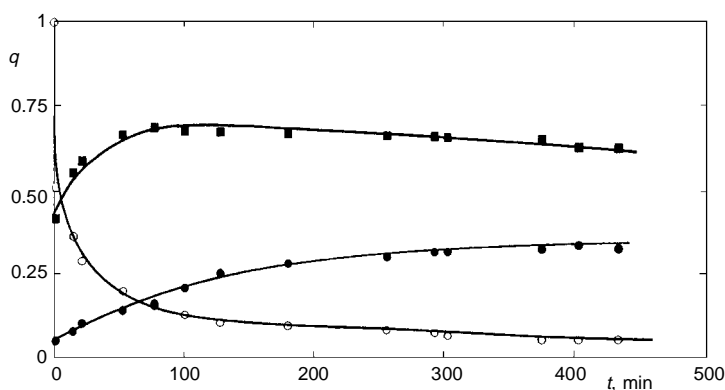

Fig. 3
Time dependence of mole fraction (q) of structurally bound ^{29}Si atoms: ○ Q^0, ■ Q^1, ● Q^2
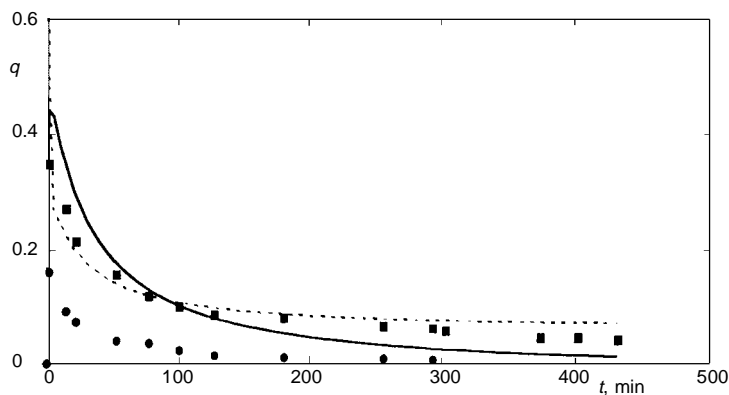

Fig. 4
Time dependence of mole fraction (q) of structurally bound ^{29}Si atoms: ■ $Q^0(0,4)$, ● $Q^0(1,3)$. Theoretical kinetic models: · · · · $Q^0(0,4)$, ——— $Q^0(1,3)$

$$d[SiOR]/dt = -k_h[SiOR][H_2O] - 1/2k_{ca}[SiOH][SiOR] \,, \tag{2}$$

$$d[SiOH]/dt = k_h[SiOR][H_2O] - 1/2k_{ca}[SiOH][SiOR] - k_{cw}[SiOH]^2, \tag{3}$$

$$d[SiOSi]/dt = k_{cw}[SiOH]^2 + k_{ca}[SiOH][SiOR] \,, \tag{4}$$

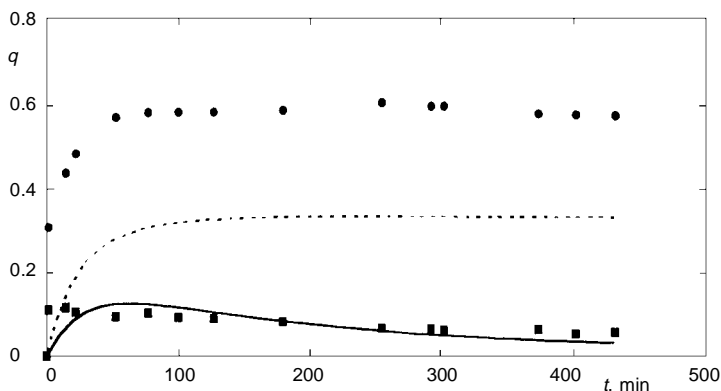FIG. 5

Time dependence of mole fraction (q) of structurally bound [29]Si atoms: ● $Q^1(0,3)$, ■ $Q^1(1,2)$. Theoretical kinetic models: · · · · $Q^1(0,3)$, ——— $Q^1(1,2)$
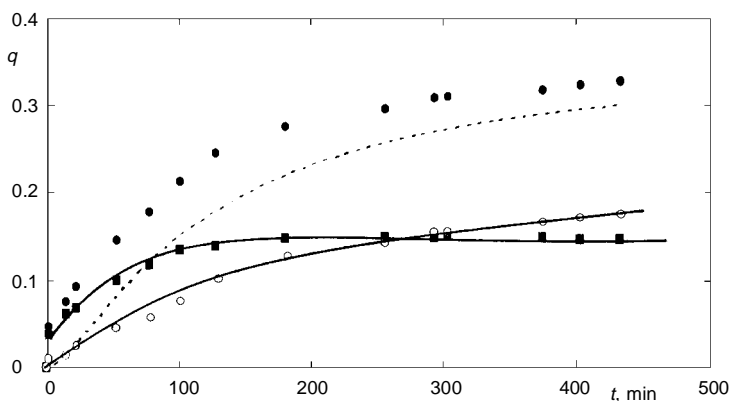
FIG. 6

Time dependence of mole fraction (q) of structurally bound [29]Si atoms: ● $Q^2(0,2)$ in cyclic plus linear oligomers, ■ $Q^2(0,2)$ in linear oligomers, ○ $Q^2(0,2)$ in cyclic oligomers, · · · · theoretical kinetic model $Q^2(0,2)$

where k_h is the hydrolysis rate constant, k_{ca} is rate constant of the condensation releasing alcohol, and k_{cw} is rate constant of the condensation releasing water. Furthermore it is presumed that the chemical reactivities of all the products of condensation and hydrolysis are the same.

The calculation of rate constants starts from highly simplifying considerations[9,10]. They are based on the presumption that the reactivity of hydroxyl and ethoxyl groups is the same throughout the reaction time and the sol–gel polycondensation itself can be divided into two separable phases. In the first several minutes the hydrolysis takes place which is then followed by polycondensation. This presumption allows us to calculate the hydrolysis rate constant k_h from a very short time interval at the beginning of the process using Eq. (2) in which the second term concerning the condensation is neglected. The condensation rate constant k_{ca} can be calculated similarly by neglecting hydrolysis in later phases of the reaction, i.e., by eliminating the first term from Eq. (2). Knowing the rate constant k_{ca}, we can calculate the constant k_{cw} from Eq. (4). It must be admitted that the calculations are loaded with a certain error, since different reactivities of hydroxyl and ethoxyl groups in various structural units make themselves felt. The rate constants gradually decreased with increasing reaction time. Table II presents the total average values of rate constants.

A quantitative evaluation of the polycondensation of TEOS can be carried out by comparing the rate constants determined for the polycondensation of our system with the literature data[10,17] concerning the polycondensation of TMOS, as it is shown in Table II. From this comparison it follows that at the given conditions the initial rate of condensation of TEOS is comparable with that of TMOS.

The theoretical time dependences of mole fractions of selected $Q^s(h,r)$ of structurally bound ^{29}Si atoms were calculated on the basis of a procedure described in literature[17] and are presented in Figs 4–6. Our experimental rate constants were adopted in the calculation. It was observed[9,10,17] that the real system shows a behaviour considerably

TABLE II
Hydrolysis (k_h) and condensation (k_{ca}, k_{cw}) rate constants of alkoxysilanes

| Constant | Alkoxysilane | | |
dm^3 mol^{-1} min^{-1}	TEOS	TMOS[a]	TMOS[b]
k_h	0.13	0.19	0.20
$k_{ca} . 10^3$	1.5 ± 0.5	2.1 ± 0.1	1.0
$k_{cw} . 10^3$	10.7 ± 0.5	4.2 ± 0.1	6.0

[a] Ref.[10]. [b] Ref.[17].

different from the theoretical presumptions. As it follows from Figs 3–6 our observations agree well with the literature data. Deviations in the behaviour of real system from the model ideas can be explained with high probability by the different reactivity of the hydrolysis products and oligomers affected by steric and inductive effects[9,10,17].

For answering the question whether small, cyclic, highly condensed building units are formed or linear polycondensation is preferred, it is necessary to evaluate the extent of the cyclization reaction during the polycondensation and compare the proportions of individual oligomers with the model ideas about distribution of polymerization degrees in the reaction mixture. The interpretation of ^{29}Si NMR spectra showed that linear products are formed in the reaction mixture first, and only later the cyclic molecules begin to be formed. Their proportion in the reaction mixture gradually increases until finally the mole fraction of structurally bound units $Q^2(0,2)$ in cyclic oligomers exceeds the mole fraction of similarly bound units in linear oligomers (Fig. 6). For the purpose of evaluation of the extent of cyclization, we defined the cyclization degree which is equal to the relation of amount of cyclic products and amount of all oligomers able of cyclization (i.e. trimers and higher oligomers). From the results it follows that the cyclization degree increases with time and the ratio reaches almost 0.30 at the end of the experiment. During the polycondensation the molar concentration of cyclic tetramer continuously increases, whereas that of the linear tetramer remains almost constant (Fig. 7). The trimer tends relatively little to the cyclization because of the deformation of bond angles in the three-membered cycle. Therefrom it is obvious that the share of cyclization increases as the polycondensation proceeds. The changes of molar concentrations of all the oligomers in the reaction mixture are depicted in the time dependences in Fig. 8.
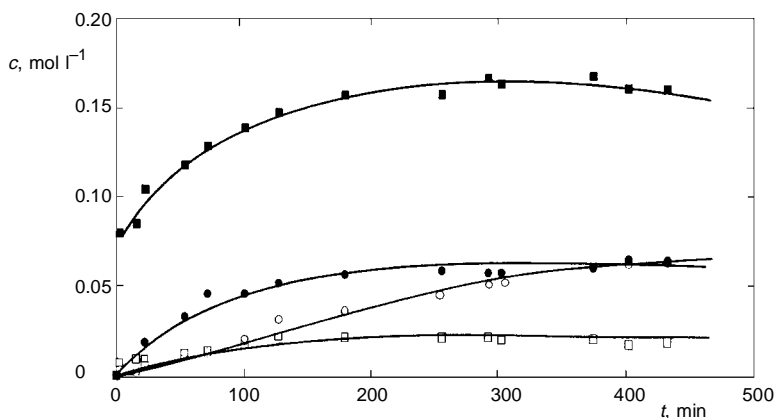

FIG. 7
Time dependence of molar concentration of oligomers: ☐ cyclic trimer, ■ linear trimer, ○ cyclic tetramer, ● linear tetramer

For evaluation of behaviour of a real system we can adopt the comparison of the mole fraction distribution of polymerization degree determined with the Flory–Stockmayer model[11], even though the basic presumptions of the Flory–Stockmayer model (viz. that the functional groups have the same reactivities independent of the magnitude of oligomer and no cyclization takes place) are not fulfilled. For comparing the real state of system with the Flory–Stockmayer model, we deliberately selected such a moment of the polycondensation when the condensation degree p had the value of 0.35 (the p value can be calculated[2] from experimental data from Eq. (5)).

$$p = (\sum_{s=1}^{4} sq_s)/f \tag{5}$$

Here q_s stands for the molefraction of structural units Q^s, s corresponds to the number of the siloxane bonds at the given Si atom, and f is the functionality of monomer (i.e., 4).

Figures 9 and 10 represent graphically the theoretical and measured mole fraction distributions of polymerization degree for a given degree of condensation ($p = 0.35$) and functionality of monomer (2 or 4). From the differences seen in the figures it follows that the reactivities of monomer and oligomer are different, and the polycondensation does not proceed statistically randomly. A distinctly lower content of monomer in the reaction mixture as compared with the expected one, and, on the other hand, a higher content of dimers, trimers, and tetramers confirm the fact that at the given conditions the monomer is substantially more reactive than the other oligomers which are formed relatively easily and rapidly but their subsequent condensation is retarded. These differences cannot be explained by reduced functionality of the monomer either,
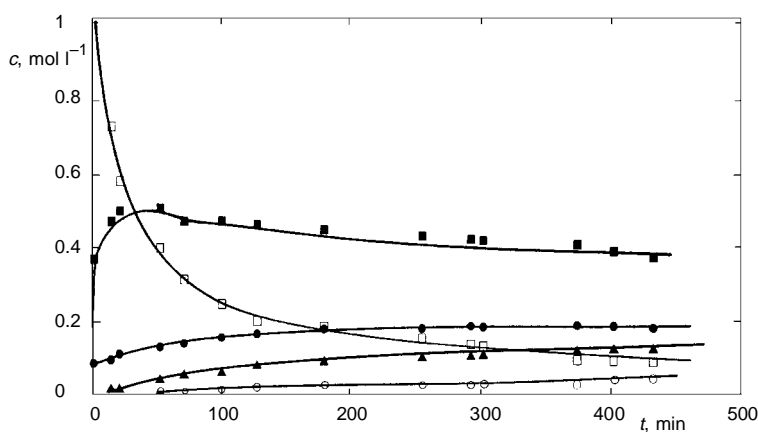

Fig. 8

Time dependence of molar concentration of oligomers: ☐ monomer, ■ dimer, ● trimer, ▲ tetramer, ❍ pentamer

since the deviations from the theoretical model are distinct with the functionality equal to 4 as well as the selected functionality of 2 which can also be presumed at the given composition of the mixture (i.e., ratio of amounts TEOS/water = 1 : 1).

It is possible to calculate[19] the real number average polymerization degree $\overline{X}_{n,exp}$ of all the oligomers from the measured mole fraction distribution of polymerization degree using the equation:
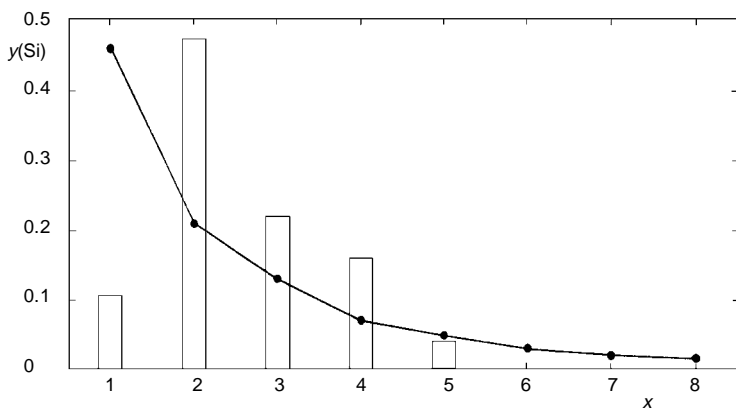

Fig. 9

Mole fraction distribution of polymerization degree at the condensation degree of 0.35 (columns) as compared with the Flory–Stockmayer model at the chosen functionality of 2 and the same condensation degree (curve and points)
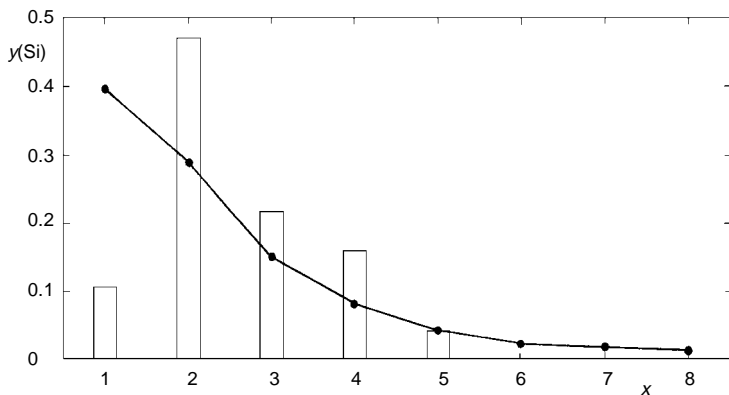

Fig. 10

Mole fraction distribution of polymerization degree at the condensation degree of 0.35 (columns) as compared with the Flory–Stockmayer model at the chosen functionality of 4 and the same condensation degree (curve and points)

$$\overline{X}_{n,exp} = \sum_i x_i y_i \ , \tag{6}$$

where y_i is the mole fraction of the oligomer with the polymerization degree x_i. Moreover it is possible to calculate[19] the theoretical number average polymerization degree $\overline{X}_n$ for the given condensation degree from Eq. (7).

$$\overline{X}_n = (1 - pf/2)^{-1} \tag{7}$$

On the basis of comparison of values of the real and the theoretical number average polymerization degrees, $\overline{X}_{n,exp} = 2.85$ and $\overline{X}_n = 3.33$, it can be stated that the growth of size of oligomers ceases after some time and they preferably undergo the cyclization. This result agrees with the fact that no oligomers higher than pentamers were found in the mixture.

CONCLUSION

The polycondensation of TEOS in acid medium with substoichiometric content of water does not proceed statistically randomly and the reactivity differences between the individual products of hydrolysis and condensation are considerable.

From the magnitude of proportion of cyclic products of polycondensation, the absence of higher oligomers, the comparison of experimentally found distribution of polymerization degrees with the Flory–Stockmayer model, and from the comparison of theoretical and experimental number average polymerization degrees it follows that, at the given conditions, the polycondensation reactions of TEOS involve high proportions of the cyclization whose importance increases in later phases of polycondensation when the mixture predominantly contains the linear tetramers and pentamers. It was confirmed that the cyclization is a dominant process which takes place during the sol–gel polycondensation with low water content in the reaction mixture where it would be possible to presume a low extent of the cyclization reactions and a higher extent of formation of linear chains. It can be expected that in a real medium, when the hydrolysis and polycondensation mainly proceed by action of humidity from atmosphere, short linear oligomers will be formed in the reaction mixture first (and these will predominantly undergo the cyclization), whereas in later phases – with increasing water content in the system – the cyclic products formed will be interconnected and will form highly condensed primary building units similar to those described in the case of polycondensation of TEOS in the presence of excess water[2]. The glassy product formed will then be formed rather by small aggregated units than by a polymeric network with entanglements of linear chains, which is presumed by some authors[12,13].

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