# STUDY OF POLYCONDENSATION OF TETRAETHOXYSILANE CATALYZED WITH DIBUTYLBIS[1-OXO(DODECYL)OXY]STANNANE USING $^{1}$H NMR AND $^{29}$Si NMR SPECTROMETRY AND QUASI ELASTIC LIGHT SCATTERING

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The polycondensation of tetraethoxysilane (TEOS) catalyzed with dibutylbis[1-oxo(dodecyl)oxy]stannane (dibutyltin dilaurate, DBTDL) has been investigated with the help of $^{1}$H and $^{29}$Si NMR spectrometry and quasi elastic light scattering (QELS). It has been found that in contrast to the acid catalyzed polycondensation the siloxane chain grows in linear and branched way, the proportion of cyclization reactions being slight. The rate of chain growth is relatively high, which is indicated by the impossibility to detect the presence of shorter oligomers in the reaction mixture by means of $^{29}$Si NMR. The found rate constant of polycondensation of TEOS catalyzed with DBTDL is $k$ = 0.052 $dm^6\ min^{-1}\ mol^{-1}$. From the determined condensation degree at the gelation point (0.20–0.35) and the ratio of consumed amount of ethoxysilane units to the consumed amount of monomer at the gelation point (0.49–0.69) it follows that the gel is predominantly formed by cross-linking of branched macromolecules, the reaction mixture containing no distinct proportions of polycyclic and highly condensed structural units. The density of network of the gel formed is relatively low, which was proved by $^{29}$Si CP/MAS NMR spectra of the solid gels. Investigation of QELS of the reaction mixture showed that the relatively large particles, microgels, were formed practically immediately after the reaction had started. The presence of such particles in the reaction mixture of acid catalyzed polycondensation of TEOS was not proved.

**Key words:** Sol–gel polycondensation; Tetraethoxysilane; Dibutylbis[1-oxo(dodecyl)oxy]stannane; NMR, $^{1}$H, $^{29}$Si, $^{29}$Si CP/MAS; QELS.

Recently, the sol–gel polycondensation of alkoxysilanes has been increasingly studied mainly for the fact that in this relatively easily controlled way it is possible to prepare very pure siliceous materials of suitable properties (the so-called CERAMERs or ORMOSILs) at current temperatures[1].

The course of acid catalyzed polycondensation of alkoxysilanes[2–4] and the structure of the oligomers formed[5,6] are described in literature relatively well. It is stated that cyclization reactions play a considerable role in such catalyzed polycondensation to produce highly condensed, polycyclic structural units whose aggregation forms a gel[7,8].

However, not only acids (most frequently HCl) are used as catalysts of the polycondensation of alkoxysilanes. Also adopted are aqueous ammonia[9–13] or sodium hydroxide[13], which act as basic catalysts of the polycondensation, or some organometallics, which act as neutral catalysts[14–16]. However, the base catalyzed polycondensation does not usually produce transparent glassy materials, leading to turbid, opaque or even powdery product instead[9,12] (formed by colloidal or precipitated siliceous particles). This nature of products is due to the nucleophilic mechanism of the polycondensation[12]. On the other hand, in the presence of organometallic catalyst the polycondensation of alkoxysilanes produces materials of glassy appearance similar to those formed in acid catalyzed polycondensation. The most frequently adopted organometallic catalyst of the polycondensation of alkoxysilanes is dibutylbis[1-oxo(dodecyl)oxy]stannane (semitrivial name dibutyltin dilaurate, DBTDL)[14,15], a compound traditionally used for cross-linking siloxane rubbers with terminal hydroxyl groups by the reaction with tetraethoxysilane (TEOS)[17–21], where the application of DBTDL to the polycondensation of alkoxysilanes alone has obviously been derived from. Although the application of DBTDL to cross-linking of siloxane rubber is relatively common, the mechanism of its catalytic action is not precisely known. The course itself of such catalyzed polycondensation of alkoxysilanes has not been described in literature even though it has a decisive effect on the structure of siloxane network and hence on resulting physical and mechanical properties of the glassy siloxane material.

The aim of this work was to follow the course of polycondensation of TEOS catalyzed with DBTDL, find the degree of condensation of the system and cross-linking at the point of gelation, evaluate the extent of cyclization reactions, try to suggest the mechanism of catalytic action of DBTDL, and determine the rate constants of sol–gel process. In the context of our previous paper[22] we want to compare the polycondensation course catalyzed with DBTDL with that in the acid catalyzed sol–gel process.

## EXPERIMENTAL

The polycondensation course of the individual reaction mixtures was monitored with the help of $^{1}H$ and $^{29}Si$ NMR spectrometry and quasi elastic light scattering (QELS). The structure of resulting gels was evaluated with the help of $^{29}Si$ CP/MAS NMR spectrometry. The reaction mixture for the $^{1}H$ and $^{29}Si$ NMR experiments was prepared by mixing TEOS ($Si(OC_2H_5)_4$; Synthesia Kolín, Czech Republic) with a solution composed of the respective amounts of deuteriated acetone ($(CD_3)_2CO$; Merck, Germany; 99.5% D) and deuterium oxide ($D_2O$; Merck, Germany; 99.5% D), and final adding DBTDL ($C_{32}H_{64}O_4Sn$; Synthesia Kolín, Czech Republic). Precise composition of the reaction mixtures is given in Table I. The volume of reaction mixtures was adjusted to the magnitude of the tubes adopted, *i.e.* always 3.2 ml for the $^{29}Si$ NMR experiments and 1.3 ml for the $^{1}H$ NMR experiments. The TEOS concentration was 2.02 mol $dm^{-3}$.

The monitoring of QELS was realized with a reaction mixture prepared similarly as No. 2 in Table I: the deuteriated acetone and deuterium oxide were replaced by normal acetone ($C_3H_6O$ p.a.; 0.5 wt.% water) and distilled water. For comparison with the course of acid catalyzed polycondensation, we also measured QELS in the reaction mixture containing hydrochloric acid (HCl with 65.0 wt.%

water) instead of DBTDL as the catalyst, using the molar ratios of TEOS : HCl : $H_2O$ : $C_3H_6O$ = 1 : 0.03 : 1 : 3.6.

The reaction mixtures used for preparation of gels for investigation of structure of solid products after the gelation point by means of $^{29}$Si CP/MAS NMR spectrometry were the same as those used for the QELS experiments.

*Parameters of measurements of NMR spectra and QELS.* The $^{29}$Si NMR spectra of the mixtures were measured in closed 10 mm glass tubes using a Bruker AM 400 FT NMR spectrometer at the frequency of 75.9 MHz with internal deuterium stabilization. The DEPT pulse sequence was adopted to increase the sensitivity. Number of data points 32K, mixing pulse $\theta = 24$, $\tau = 142$ ms, number of FID accumulations 32, repetition delay 5 s, temperature 303 K. The $^{29}$Si scale was calibrated with hexamethyldisiloxane (HMDS) as the standard. The chemical shift of $^{29}$Si in HMDS is 6 ppm against tetramethylsilane (TMS).

The $^1$H NMR spectra were measured in closed 5 mm glass tubes with the above-mentioned apparatus at the frequency of 400.1 MHz. The number of FID accumulations was 8, temperature 303 K, repetition delay 5 s. The $^1$H scale was calibrated with internal TMS where the chemical shift of $^1$H has the value of 0 ppm.

The $^{29}$Si CP/MAS NMR spectra were measured in closed 7 mm ZrO cells with a Bruker DSX 200 FT NMR spectrometer at the frequency of 39.75 MHz. The number of data points 6K, repetition delay 15 s, contact time 5 ms, number of FID accumulations 640 and 4 800 for the products prepared by acid catalyzed and DBTDL catalyzed processes, respectively. The $^{29}$Si scale was calibrated with the help of external $M_8Q_8$ standard.

The QELS measurements were carried out with an apparatus constructed at the Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic. The wavelength of radiation of the laser employed was 514.5 nm, time of duration of one experiment was 30 s, temperature 298 K. The scattering angle was 45, 60, 90, and 120°.

## RESULTS AND DISCUSSION

The investigation of polycondensation of TEOS catalyzed with DBTDL with the help of $^{29}$Si NMR started from our findings given in the previous paper[22] dealing with the course of acid catalyzed polycondensation of TEOS and optimizing the parameters of $^{29}$Si NMR spectra measurements with DEPT pulse sequence and carrying out their qualitative and quantitative interpretation. However, in contrast to the acid catalyzed system, it was almost impossible to follow the course of polycondensation of TEOS catalyzed with DBTDL by means of $^{29}$Si NMR spectrometry. No signals except for the single one due to the TEOS monomer could be found in the spectra. During the reaction, we only monitored the intensity decrease of the signal of structurally bound $^{29}$Si in TEOS with the chemical shift value of –82.01 ppm (Fig. 1). An automatic treatment of sets of $^{29}$Si NMR spectra of the individual reaction mixtures allowed a quantitative monitoring of the concentration decrease of the monomer during the polycondensation (Fig. 2). At the same time it was possible to determine the amount of the monomer consumed at the gelation point (Table I).

As the gel is formed relatively quickly, *e.g.* 80 min after preparing the mixture (see No. 4 mixture), it is certain that a relatively fast reaction takes place in the system. The fact that it was impossible to follow the formation of any other structural units contain-

ing more than one Si atom can probably be explained by a rapid formation of relatively large formations approaching to a solid in their properties. Most probably they are microgels in which there occurs a very fast transversal, spin–spin relaxation process during NMR spectral measurements at the given conditions. Due to that the magnetization change in the sample after the radiofrequency pulse vanishes sooner than it can be detected by the induction coils of the probe. This explanation is supported by the slight opalescence observed in the reaction mixture during the reaction course which indicates the presence of particles able of scattering visible light. This opalescence was observed almost immediately after preparing the reaction mixture. Also any reduction of the

TABLE I

Initial composition of reaction mixtures, values of consumed amounts of ethoxysilane groups and consumed monomer at the point of gelation $t_g$, their ratio, and the attained degree of condensation $p$. The content of individual components in mixtures is expressed in molar ratios

| Mixture No. | Molar ratios | | | $C_2H_5OSi$– mole % | TEOS mole % | $C_2H_5OSi$–/TEOS | $t_g$ min | $p$ |
|---|---|---|---|---|---|---|---|---|
| | TEOS/$D_2O$ | TEOS/DBTDL[a] | TEOS/$C_3D_6O$ | | | | | |
| 1 | 1/0.8 | 1/0.03 | 1/3.6 | 22 | 45 | 0.49 | 250 | 0.22 |
| 2 | 1/1 | 1/0.03 | 1/3.6 | 24 | 48 | 0.50 | 150 | 0.24 |
| 3 | 1/1.5 | 1/0.03 | 1/3.6 | 30 | 58 | 0.52 | 130 | 0.30 |
| 4 | 1/2 | 1/0.03 | 1/3.6 | 35 | 69 | 0.51 | 110 | 0.35 |
| 5 | 1/0.8 | 1/0.05 | 1/3.6 | 20 | 40 | 0.50 | 80 | 0.20 |
| 6 | 1/1 | 1/0.015 | 1/3.6 | 24 | 45 | 0.53 | 210 | 0.24 |

[a] DBTDL dibutyltin dilaurate.

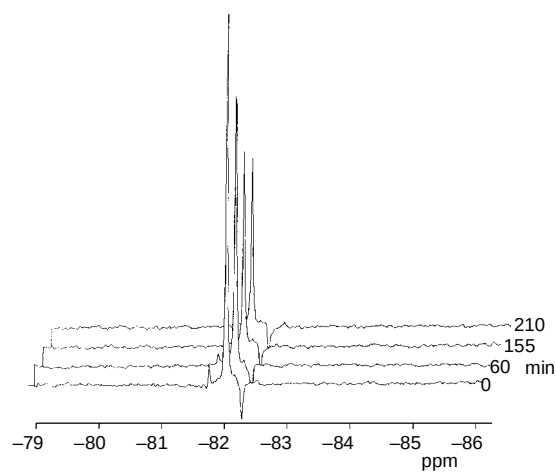



FIG. 1

$^{29}$Si NMR spectra of reaction mixture No. 2 (Table I) measured at various reaction times

catalyst and water amounts in the reaction mixture, *i.e.* lowering of the polycondensation rate, did not enable us to follow anything else than the TEOS decrease.

Examining the composition of system by means of $^1$H NMR spectrometry, we found that relatively soon were formed linear and branched chains of macromolecules whose cross-linking and entanglement led to the gel. Application of $^1$H NMR spectrometry makes it possible to determine the content of ethoxysilane groups in TEOS and the siloxane polymers as well as the content of ethoxyl groups corresponding to the ethanol released (Figs 3 and 4). The $CH_3CH_2OSi\equiv$ group is characterized by a quartet with the chemical shift values of 3.829, 3.811, 3.794, and 3.776 ppm and coupling constant $^2J$(H,H) = 7 Hz ($-CH_2-$), and by a triplet 1.205, 1.118, 1.171 ppm ($-CH_3$). The mole-

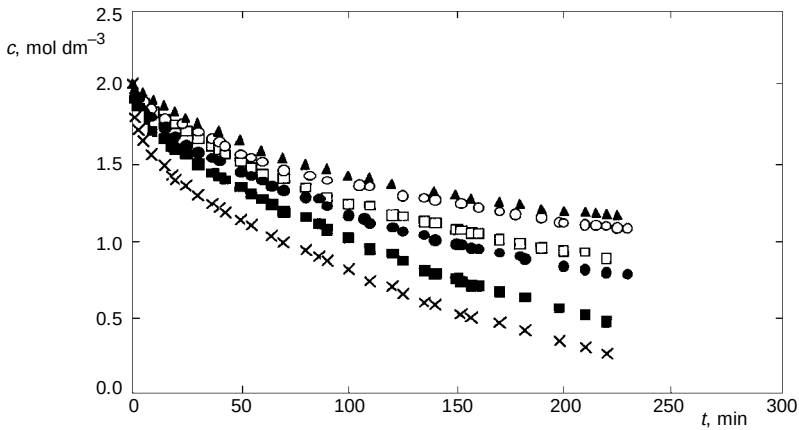



FIG. 2
Time dependence of molar concentration of TEOS in reaction mixtures 1–6 (Table I): ▲ No. 1, ❒ No. 2, ■ No. 3, × No. 4, ● No. 5, ❍ No. 6

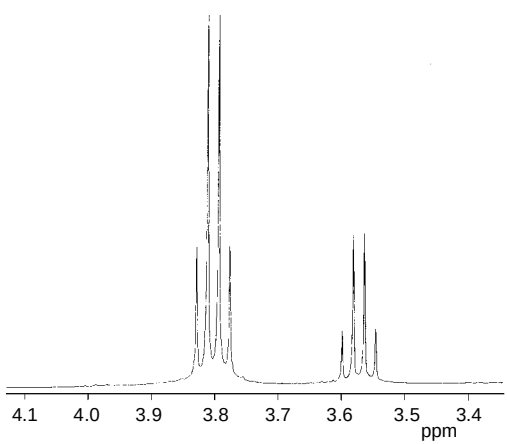



FIG. 3
$^1$H NMR spectrum in the region of resonance of $-CH_2-$ groups in reaction mixture No. 2 after 108 min of reaction

cule of released ethanol $CH_3CH_2OD$ is characterized by a quartet 3.598, 3.580, 3.562, 3.545 ppm ($–CH_2–$) and a triplet 1.151, 1.133, 1.116 ppm ($–CH_3$). For the purpose of quantitative monitoring of the polycondensation course we chose the signals of $–CH_2–$ groups which are well separated. Their comparison enables one to follow the decrease of ethoxysilane groups during the polycondensation. It was proved that the ratio of sum of integral intensities of signals of $–CH_2–$ protons in the $CH_3CH_2OSi\equiv$ group and in $CH_3CH_2OD$ molecule to the integral intensity of the reference signal of $–CH_3$ protons of residual acetone, which does not take part in the reaction, is constant throughout the process. Thus *e.g.* in reaction mixture No. 2 the average value of this ratio was 0.0237 during the whole period of monitoring of the polycondensation course, the value of standard deviation (which represents a measure of accuracy of maintaining of $^1$H NMR signal in all the $–CH_2–$ groups) being $\sigma_{n-1} = \pm 0.0002$ (or expressed in per cent: ±0.88%). Therefrom it is obvious that the signals given represent all the protons of $–CH_2–$ groups and that no losses of signal occur during the polycondensation and gelation. Hence the evaluation given describes quantitatively accurately the course of sol–gel process. With regard to the fact that in the $^{29}$Si NMR spectra no signals were found which would indicate hydrolysis products (the latter most probably condense very fast to give macromolecules and microgels), it is obvious that the decrease in $CH_3CH_2OSi\equiv$ groups corresponds with the formation of $\equiv Si–O–Si\equiv$ bonds. Therefrom it follows that the decrease of ethoxysilane groups also directly corresponds to the degree of condensation in the system. Table I gives the values of the consumed amount of ethoxysilane groups and the condensation degree attained at the point of gelation.

The values of Table I indicate that the gel is probably formed by linking of little branched siloxane molecules, and it has a nature of relatively thin polymeric network as

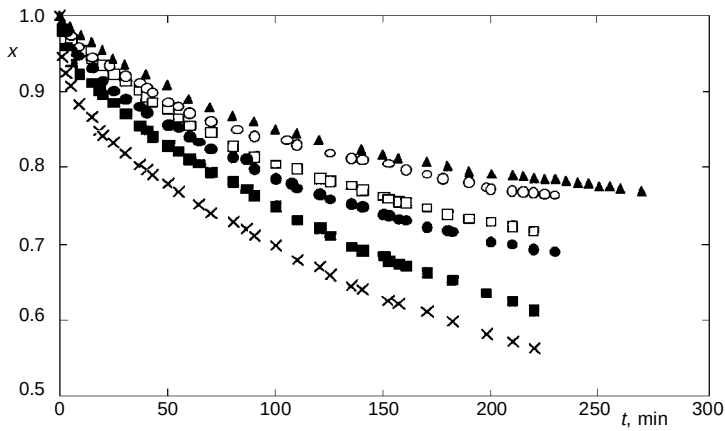



FIG. 4

Time dependence of molar fraction of $CH_3CH_2OSi\equiv$ groups in reaction mixtures 1–6 (Table I.): ▲ No. 1, ❒ No. 2, ■ No. 3, × No. 4, ● No. 5, ❍ No. 6

compared with the gel produced by the acid catalyzed polycondensation. An important finding, too, is the fact that the condensation degree of system found by us at the point of gelation (0.22–0.35) is substantially lower than that given in refs[7,23] for the reaction mixture at the point of gelation in acid catalyzed polycondensation (0.81). The latter value was explained[7,8] by a formation of primary highly condensed polycyclic building units containing eight to ten Si atoms which form a gel only later. On the basis of the results obtained it can be presumed that the polycondensation of TEOS catalyzed with DBTDL is not accompanied by any significant cyclization reactions and, hence, formation of the polycyclic building units mentioned, as it is the case in acid catalyzed polycondensation of TEOS. The above-mentioned presumptions were confirmed by comparing the $^{29}$Si CP/MAS NMR spectra of the solid products formed by the polycondensation of TEOS catalyzed with HCl and DBTDL (Fig. 5). For quantitative evaluation of content of individual structurally bound $^{29}$Si atoms in solid samples it was necessary to determine the dependence of signal intensity on the contact time value and standardize the integral intensities obtained according to this dependence. In spite of that, the values given are of orientational nature only. From the spectra it followed that the gel prepared by the polycondensation catalyzed with DBTDL is both qualitatively and quantitatively different, containing a substantially higher amount of linear structural units than the gel prepared by the acid catalyzed process. The product of DBTDL catalyzed polycondensation exhibits the ratio of structural units $Q^1/Q^2/Q^3/Q^4$ = 1.6/2/1.6/1 (condensation degree $p$ = 0.53), whereas the product of acid catalyzed process only contains three structural units whose ratio is $Q^1/Q^2/Q^3/Q^4$ = 0/1/5.2/3 (condensation degree $p$ = 0.80), which very well corresponds to literature data[7,8]. The structure of gel is also markedly different from those after base catalyzed polycondensation ($Q^1/Q^2/Q^3/Q^4$ = 5/5/5/18) and noncatalyzed polycondensation of TEOS ($Q^1/Q^2/Q^3/Q^4$ = 14/15/23/33, ref.[24]). It is very important that the gel prepared by the

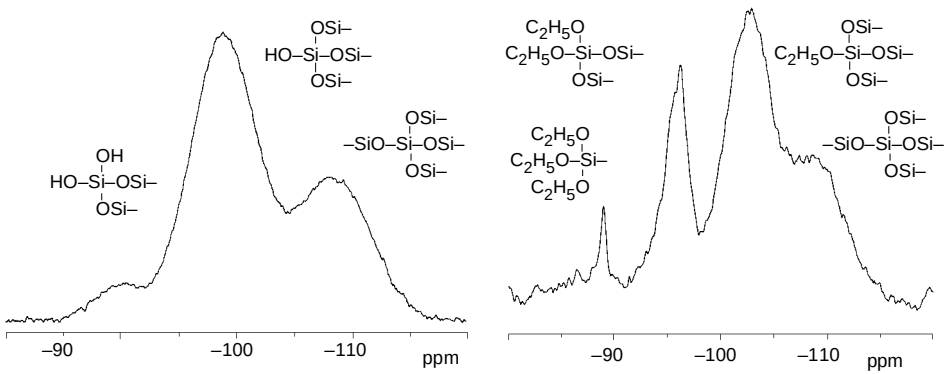



FIG. 5

$^{29}$Si CP/MAS NMR spectra of solid gels. Left – spectrum of gel from acid catalyzed polycondensation, right – spectrum of gel from polycondensation of TEOS catalyzed with DBTDL

polycondensation catalyzed by DBTDL contains only ethoxyl groups and, on the other hand, the gel prepared by the acid catalyzed process contains only hydroxyl groups (*cf.* Fig. 5). This confirms our presumption that products of hydrolysis condense very fast and the decrease of concentration of $CH_3CH_2OSi\equiv$ corresponds with the formation of ≡Si–O–Si≡ bonds. It must be mentioned, however, that the values in Table I concern the presumed state of system at the point of gelation, whereas the structure of solid gel prepared by the polycondensation of mixture No. 2 was determined – with respect to the big time demands of the experiment – in the time interval $t = 10–17\ t_g$, hence distinctly after the point of gelation. (Q stands for the four-functional structural unit and the index denotes the number of siloxane bonds to the given Si atom.)

From the $^1H$ and $^{29}Si$ NMR spectra it also follows that the degree of condensation of the system and the density of network at the point of gelation slightly increase with increasing water content in the reaction mixture. These values are, on the other hand, independent of the DBTDL content in the mixture. Therefrom it is obvious that DBTDL does not operate as a cross-linking agent (which would be chemically bound to the network being formed) in the polycondensation course but it acts as a catalyst or initiator of the polycondensation of TEOS. Literature presents several suggestions of mechanism of the role of DBTDL in cross-linking of siloxane rubbers with terminal hydroxyl groups, some of them presuming incorporation of DBTDL directly into the network being formed[25,26]. In the context of the above-mentioned findings we consider the mechanism suggested by Weij[27] to be the most acceptable: it presumes the hydrolysis of DBTDL as the first step releasing lauric acid. The hydrolysate formed reacts with TEOS, and ethanol is set free. The compound formed involves the ≡Sn–O–Si≡ bond which is supposed to be easily cleaved in silanolysis by the hydroxyl terminal of siloxane rubber to form the ≡Si–O–Si≡ bond with regeneration of the catalytically active compound – hydroxydibutyltin laurate.

In the case of homopolycondensation of TEOS, however, the situation can be similar to a certain extent only. When looking for the mechanism of catalytic action of DBTDL, one must start from the findings following from the $^{29}Si$ NMR experiments and the fact that no hydrolysis products from TEOS nor formation of any oligomers nor polycondensation intermediates could be revealed by the $^{29}Si$ NMR spectra, whereas these compounds were unambiguously proved in both acid and base catalyzed polycondensations at comparable conditions[22,24].

The absence of hydrolysis products can be interpreted either by the absence of hydrolysis in the polycondensation (no hydrolysis product are formed at all), or the hydrolysis product are formed and are so unstable at the given conditions (*i.e.* they are condensed very fast) that their actual concentration is very low. With regard to the fact that at certain conditions (low water content) the hydrolysis products need not be detectable by $^{29}Si$ NMR spectrometry even in acid catalyzed polycondensation[4], we are inclined to accept the latter interpretation above. The absence and nondetectability of

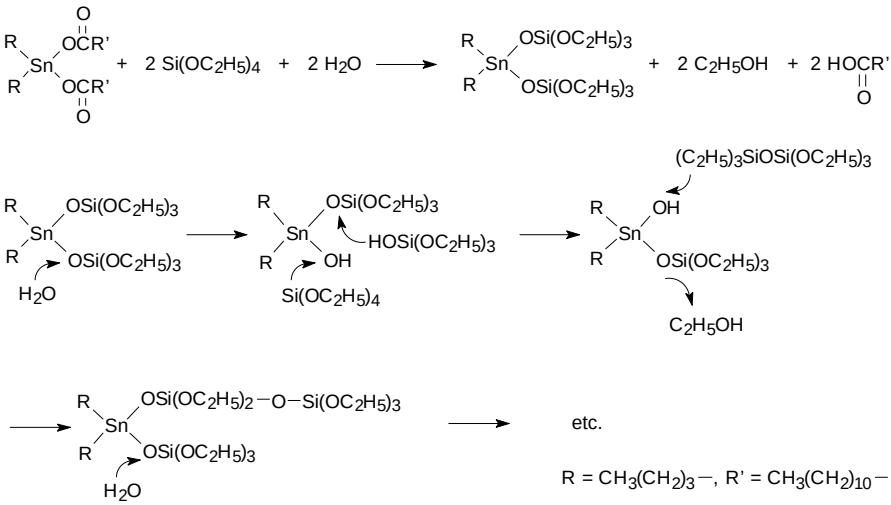
polycondensation intermediates is obviously connected with the process mechanism itself and with its high speed. However, the $^{1}H$ and $^{29}Si$ NMR experiments showed that the overall decrease of neither the monomer nor ethoxysilane groups is distinctly abrupt. Therefrom it follows that the proper very fast hydrolysis and condensation only occurs near the DBTDL molecules which, due to their bulkiness, are substantially less mobile than the proton catalyst in the acid catalyzed polycondensation. That, obviously, is why the oligomers formed are immediately and constantly introduced into the reaction of polymer growth, which results in the absence of shorter oligomers (dimers, trimers, ...) from the reaction mixture.

Although the above-mentioned experiments do not enable one to precisely follow the mechanism of catalytic action of DBTDL in the polycondensation, one can presume that the hydrolysis of DBTDL is the first step. The compounds formed react in the subsequent step with a TEOS molecule to form the ≡Sn–O–Si≡ bond. In contrast to cross-linking of siloxane rubbers, however, silanolysis cannot be the next step since the reaction mixture contains no hydroxysilanes. But the hydrolysis of the ≡Sn–O–Si≡ bond sets free $HO–Si(OC_2H_5)_3$, and this compound must undergo fast condensation since its signal is absent from the $^{29}Si$ NMR spectra. We presume that condensation is realized by silanolysis of another ≡Sn–O–Si≡ bond in analogy to cross-linking of siloxane rubbers. Since no oligomers were identified either, we presume that the intermediate formed reacts practically immediately with the ≡Sn–OH group formed to regenerate the ≡Sn–O–Si≡ bond. This group can now be hydrolyzed and the hydrolysate produced will react with another ≡Sn–O–Si≡ group with concomitant chain lengthening or branching, or it will react with the hydroxysilane set free, again with concomitant chain lengthening. Rapid repetition of these steps will result in formation and growth of the polymer. With increasing magnitude of oligomers their mobility decreases, and the growing chain will always be localized near the organometallic compound. If we admitted that both functional groups of DBTDL could participate in the reaction, then the hydrolysis and the condensation would take place at random either at one or at the other ≡Sn–O–Si≡ bond. This would considerably shorten the necessary life time of hydroxysilane molecule between its formation and subsequent condensation. The mechanism suggested is presented in the Scheme 1.

As TEOS is a four-functional monomer, it is certain that also the central parts of molecules will take part in the reactions of polymer growth with concomitant branching and cross-linking. However, from the comparison of $^{29}Si$ CP/MAS NMR spectra it followed that the extent of such condensation and branching was smaller when compared with the acid catalyzed process.

The above-mentioned mechanism is supported by monitoring the broad signal in the region of 10.5 ppm (which is due to the relatively mobile proton of carboxylic group in lauric acid) and another broad signal about 3.0 ppm (due to a hydroxyl proton, probably in the ≡Sn–OH group) in the $^{1}H$ NMR spectrum. The spectrum was measured with a

mixture obtained by washing the solid gel with hexadeuterioacetone. This gel was prepared from reaction mixture No. 2 containing no deuteriated solvents but only water and acetone.




SCHEME 1

With regard to the observed signal of carboxylic proton and the fact that no gel is formed while employing the catalytic effects of lauric acid alone, it is likely that lauric acid does not take part in the polycondensation process or its effect is negligible.

Starting from the above-mentioned considerations about the mechanism of polycondensation of TEOS catalyzed with DBTDL, we can – in the first approximation not considering the catalyst influence – describe the polycondensation course by the following summary equation:

$$n\ \mathrm{Si(OC_2H_5)_4} + (n-1)\ \mathrm{H_2O} \rightarrow$$

$$\rightarrow\ \mathrm{(C_2H_5O)_3Si[OSi(OC_2H_5)_2]_{\mathit{n}-2}OSi(OC_2H_5)_3} + (2n-2)\ \mathrm{C_2H_5OH}\ . \qquad (A)$$

For the formation of a polymer with high polymerization degree the equation can be simplified to the form:

$$n\ \mathrm{Si(OC_2H_5)_4} + n\ \mathrm{H_2O} \rightarrow -\mathrm{[OSi(OC_2H_5)_2]_{\mathit{n}}}- + 2n\ \mathrm{C_2H_5OH}\ . \qquad (B)$$

The basic step of polycondensation during the growth and formation of polymer chain then can be described as follows:

$$\mathrm{Si(OC_2H_5)_4} + \mathrm{H_2O} \rightarrow -\mathrm{[OSi(OC_2H_5)_2]}- + 2\ \mathrm{C_2H_5OH}\ . \qquad (C)$$

The last equation (*C*) can be considered valid also in such cases where the hydrolysis of ethoxyl groups will also take place at the end of the growing chain and the condensation will occur between two hydroxyl groups. At the same time, also in such a case where the catalytic action of DBTDL is involved in the reaction. This kinetic model can be simplified by neglecting the initial hydrolysis of DBTDL in the calculation of rate constants. If the role of DBTDL in the polycondensation of TEOS is viewed as homogeneous catalysis, then the polycondensation kinetics can be described by Eq. (*1*).

$$-\mathrm{d}[\mathrm{Si(OC_2H_5)}]/\mathrm{d}t = k[\mathrm{DBTDL}][\mathrm{Si(OC_2H_5)}][\mathrm{H_2O}] \qquad (1)$$

As the DBTDL content can be considered constant throughout the polycondensation, the process given is transformed formally into a second order reaction with the rate constant $k'$ expressed as $k' = k[\mathrm{DBTDL}]$. The polycondensation kinetics is then described by the following expression:

$$-\mathrm{d}[\mathrm{Si(OC_2H_5)}]/\mathrm{d}t = k'[\mathrm{Si(OC_2H_5)}][\mathrm{H_2O}] \; . \qquad (2)$$

Analytical solution of this differential equation for the individual mixtures gave the values of the polycondensation rate constants $k'$. The values of rate constants were calculated by the method of the initial rates determined from the first $^1$H NMR spectrum measured after the start of reaction. Table II presents the values of the $k$ and $k'$ rate constants obtained.

In order to confirm the above-mentioned presumptions about fast formation of macromolecules and microgels, we carried out QELS measurements in a system in which a polycondensation of TEOS catalyzed with DBTDL took place. This also enabled us to estimate the magnitude of scattering particles, and using the time dependence of this magnitude we could follow the polycondensation course till the gelation time.

TABLE II
Rate constants $k$ and $k'$ calculated for polycondensation of reaction mixtures and average rate constant $k$

| Mixture No. | $k$, $\mathrm{dm^6\ min^{-1}\ mol^{-2}}$ | $k'$, $\mathrm{dm^3\ min^{-1}\ mol^{-1}}$ |
|---|---|---|
| 1 | 0.0521 | $2.97 \pm 0.03 \,.\, 10^{-3}$ |
| 2 | 0.0505 | $2.95 \pm 0.01 \,.\, 10^{-3}$ |
| 3 | 0.0517 | $2.98 \pm 0.05 \,.\, 10^{-3}$ |
| 4 | 0.0525 | $2.92 \pm 0.05 \,.\, 10^{-3}$ |
| 5 | 0.0539 | $5.49 \pm 0.06 \,.\, 10^{-3}$ |
| 6 | 0.0525 | $1.95 \pm 0.05 \,.\, 10^{-3}$ |
| Average | $0.0522 \pm 0.0012$ | |

It must be emphasized here that, in contrast to the measurements of classical light scattering, only the QELS measurements can provide an estimate (at least in the order of magnitude) of magnitude of the scattering particles whose mass concentration is unknown and – in addition to it – keeps changing. But not even the QELS measurements can provide exact values of the hydrodynamic radius of the scattering particles, and the values obtained are orientational only. That is why we carried the QELS measurement in a system containing hydrochloric acid as the catalyst of polycondensation of TEOS, which provided data for mutual comparisons.

The shapes of correlation lines given in Figs 6 and 7 show perceptible differences following from different magnitudes of the particles and their population in the system. The distribution curves in Figs 8 and 9 then express these differences by the dependence of intensity of the scattered radiation on the hydrodynamic radius of particle. In this way it was confirmed that there are almost no scattering particles present in the acid catalyzed system, the hydrodynamic radius of the particles found being about 1 nm. In

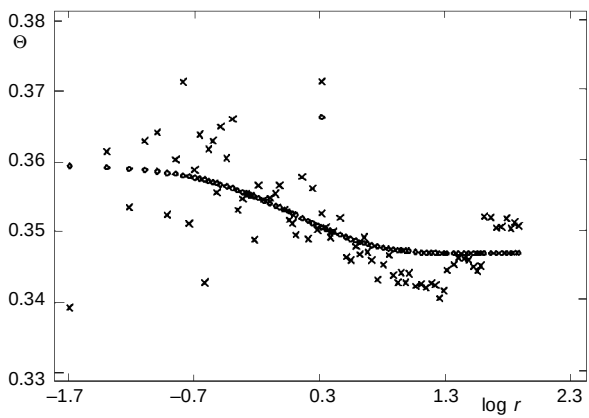



FIG. 6
Correlation curve measured for reaction mixture TEOS/$H_2O$/$C_3H_6O$/HCl after 30 days of reaction: × experimental values, ✧ regression. Dependence of intensity of scattered light Θ on hydrodynamic radius of scattering particle *r* (in nm)

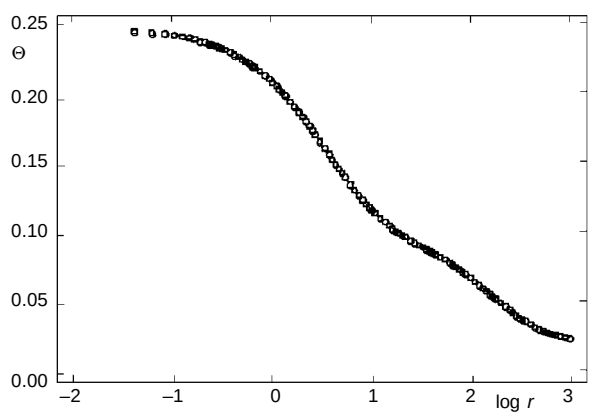



FIG. 7
Correlation curve measured for reaction mixture TEOS/$H_2O$/$C_3H_6O$/DBTDL after 20 min of reaction: × experimental values, ✧ regression

contrast to this, the system containing DBTDL as the catalyst shows two main regions, the values of maxima lying in the intervals of 3–100 and 50–1 000 nm. The value of the maxima gradually increases with time (Fig. 10). We presume that the value of hydrodynamic radius of the first maximum corresponds with the magnitude of the primary particles formed. The presence of the second maximum is not fully understood and is obviously connected with the presence of bigger structures in the system (aggregates of the particles formed, solvates and associates). As our measurements became less and less exact and certain with time, and the scattering of the values obtained increased very much, the largest safely determined hydrodynamic radius of particle before the point of gelation corresponding to the region of the first distribution maximum is about 35 nm.

These experiments have confirmed a fast formation of relatively large particles during the polycondensation of TEOS catalyzed with DBTDL and proved that scattering particles are practically absent from the system containing HCl as the catalyst.

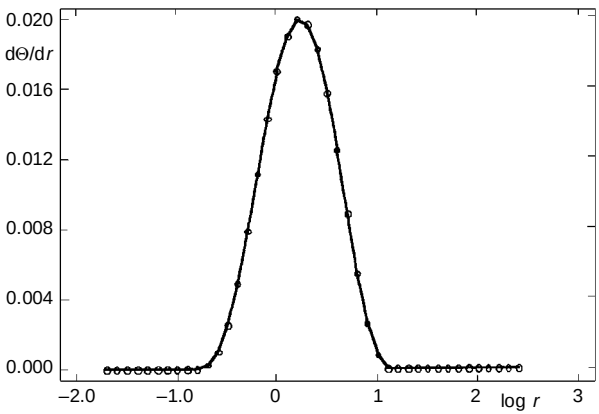



FIG. 8
Differential distribution of hydrodynamic radius *r* (nm) calculated from correlation curve in Fig. 6

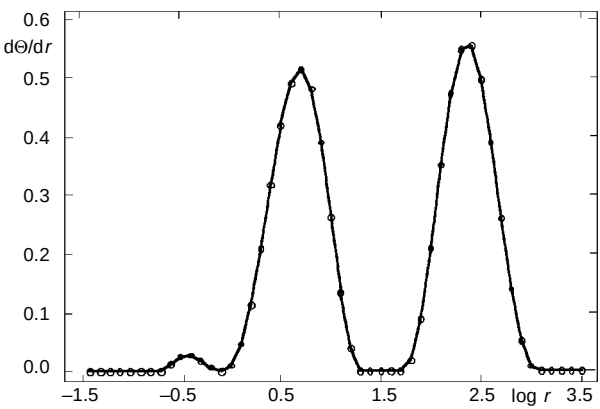



FIG. 9
Differential distribution of hydrodynamic radius *r* (nm) calculated from correlation curve in Fig. 7

Table III presents a summary of some values indicating and confirming the marked difference in the mechanisms of polycondensation of TEOS catalyzed with DBTDL or HCl.

On the basis of the experiments carried out it is possible to draw the following conclusions:

*1.* The course, mechanism and kinetics of polycondensation of TEOS catalyzed with DBTDL are distinctly different from those of TEOS polycondensation catalyzed with hydrochloric acid. With respect to the condensation degree attained and the ratio of ethoxysilane groups consumed to the monomer consumed at the point of gelation it is obvious that the dominant process in the polycondensation of TEOS catalyzed with DBTDL is the linear growth and branching of the polymeric chain and hence, in contrast to the acid catalyzed process, the cyclization reactions occur to a slight extent

TABLE III
Values characterizing differences in mechanism of polycondensation of TEOS determined for reaction mixtures of the following composition ratios: TEOS/DBTDL (or HCl)/$H_2O$/$C_3H_6O$ = 1/0.03/1/3.6

| Catalyst | $p^a$ | $p$(s)$^b$ | $Q^1/Q^2/Q^3/Q^4$[c] | $t_g$[d] | ρ[e] |
|---|---|---|---|---|---|
| DBTDL | 0.24 | 0.53 | 1.6/1/1.6/1 | 150 min | 1.75 |
| HCl | 0.81[f] | 0.80 | 0/1/5.2/3 | 40 days | 1.94 |

[a] $p$ Condensation degree at the point of gelation determined by means of $^1$H and $^{29}$Si NMR spectrometry; [b] $p$(s) condensation degree of solid gels determined by means of $^{29}$Si CP/MAS NMR spectrometry; [c] structure of solid gels determined by means of $^{29}$Si CP/MAS NMR spectrometry; [d] gelation time of the mixture; [e] ρ (g cm$^{-3}$) density of solid gel; [f] refs[4,23].

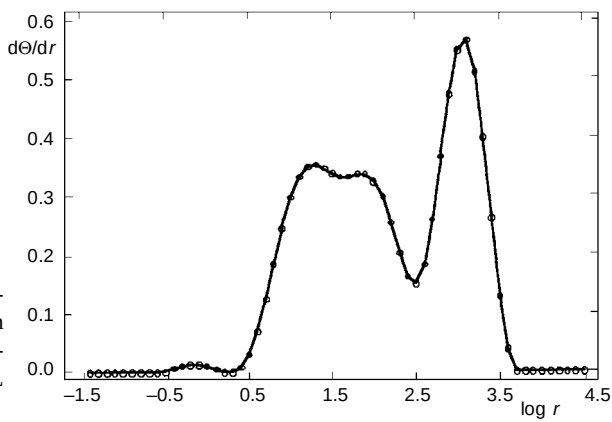



FIG. 10
Differential distribution of hydrodynamic radius $r$ (nm) calculated from correlation curve measured for mixture TEOS/$H_2O$/$C_3H_6O$/DBTDL after 100 min of reaction

only. The gel produced is built by entaglements and cross-linking of relatively large macromolecules.

*2*. The rapid formation of relatively large particles in the reaction mixture was confirmed by QELS measurements which also proved the absence of scattering particles from the reaction mixture containing HCl as the catalyst.

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