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Copolymerization of tetraethoxysilane and dimethyl(diethoxy)silane studied by ^{29}Si NMR and ab initio calculations of ^{29}Si NMR chemical shifts

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Abstract

Copolymerization of tetraethoxysilane (TEOS) and dimethyl(diethoxy)silane (DMDEOS) was studied by means of the ^{29}Si NMR spectroscopy and ab initio quantum chemical calculations. ^{29}Si NMR spectra of reaction mixtures of TEOS and DMDEOS were effectively measured by a slightly modified DEPT experiment, in which the pulse sequence is divided into two parts and all pulses on protons are replaced by selective pulses. Quantum chemical ab initio calculation of structures and ^{29}Si NMR chemical shifts of some reaction products were used in signal assignment. The assignment of the signals to corresponding structure units is not yet unambiguous; however, a semiquantitative analysis of relations in the reaction mixture of TEOS and DMDEOS could be done. Although the reactivity of the DMDEOS monomer is much higher in comparison with TEOS, the arising gel is not strictly phase separated and copolymerization of both monomers occurs. In the first stages of the process, resulting oligomers are composed of 70% of DMDEOS structure units. In the final stages of polycondensation, domains of the TEOS structure units are formed, which can act as linking units between cyclic oligomers. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Alkyalkoxysilanes; ^{29}Si NMR; Ab initio calculation

1. Introduction

Copolymerizations of different types of alkoxysilane and alkyl(alkoxy)silane monomers are industrially important reactions for obtaining the hybrid inorganic–organic materials [1–3]. It is well known that the steric and inductive effects of various substituents affect the reactivity of monomer dramatically [4,5], e.g. the reactivity of methyl(triethoxy)silane or vinyl(triethoxy)silane is much higher than the reactivity of tetraethoxysilane (TEOS) [6]. However, recent studies did not confirm formation of phase-separated systems, rather statistic copolymerization is assumed [1–3]. ^{29}Si NMR spectrometry is used with great advantage for the study of kinetics and mechanism of polycondensation of alkoxysilanes. By using polarization transfer from the neighboring spin–spin coupled proton to ^{29}Si nucleus, many problems following from very long longitudinal relaxation time T_1(^{29}Si), low sensitivity and negative NOE of ^{29}Si are overcome. Thus, INEPT and DEPT techniques made it possible to perform many detailed studies of kinetics and mechanism of polycondensation of alkoxysilanes [7–11], and also two-dimensional (2D) correlation experiments (2D ^{29}Si–^{29}Si INEPT DQF COSY) [12] with natural isotopic abundance of ^{29}Si (4.5%). In this way, the connectivity of siloxane chains and the structure of products originating in the reaction were described. ^{29}Si NMR spectroscopy together with SAXS made it possible to describe the kinetics and mechanism of the acid-catalyzed polycondensation of TEOS and tetramethoxysilane (TMOS) as well as the structure of small building units [6,13–15]. However, similar studies of copolymerization of alkoxysilanes and alkyl(alkoxy)silanes, comparable to the aforementioned detailed studies of homopolycondensation of TEOS or TMOS describing the early stages of the reaction, were not performed. Owing to that fact, the structure of small structure units forming during the early stages of copolymerization is not yet known.

The aim of the present work was: (i) to find optimum parameters of NMR experiment (DEPT), which can be used for the observation of polycondensation of mixture of TEOS and dimethyl(diethoxy)silane (DMDEOS), a system with large difference in coupling constants $J_{(1H-29Si)}$; (ii) to describe the structure of primary building units of the gel using ab initio

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calculations of optimal geometries and corresponding values of ^{29}Si NMR chemical shifts; (iii) to evaluate the extent of self-condensation, copolymerization, and cyclization in a mixture of TEOS and DMDEOS considering the cyclic products as a possible basis for formation of small building units in siloxane materials.

2. Experimental

2.1. Materials

The reaction mixtures (0.6 ml) were prepared by adding distilled water and concentrated HCl (HCl content 34% w/w) to a mixture of TEOS and DMDEOS (TEOS—Synthesia Kolin, Czech Rep.; DMDEOS—Wacker-Chemie GmbH., Germany), ethanol (Merck, Germany, 0.1% w/w water) and 0.1 ml deuterated ethanol (Merck, Germany, 99.6% D). The total composition of reaction mixtures in mole ratios was: (a) DMDEOS/H_2O/EtOH/HCl = 1/0.5/4.5/0.003; (b) TEOS/DMDEOS/H_2O/EtOH/HCl = 0.5/0.5/0.75/4.5/0.003.

2.2. ^{29}Si NMR spectroscopy

^{29}Si NMR spectra were measured in 5 mm glass tubes using a NMR spectrometer Bruker DPX 300 at the frequency of 50.6 MHz with an internal deuterium lock. The modified DEPT pulse sequence was used to increase the sensitivity of measurement. (For detailed analysis, description and optimization of experimental parameters, see later.) The number of data points was 32 K, relaxation delay 5 s, temperature 300 K and the number of FID accumulations was 16–128. An external standard, hexamethyldisiloxane (HMDS) was used for calibration of ^{29}Si scale, the chemical shift of ^{29}Si having the value of 6 ppm referred as tetramethylsilane (TMS).

2.3. Ab initio calculation of molecular structures and ^{29}Si NMR chemical shifts

The calculations were run on SGI workstations using GAUSSIAN 94 program package [16]. Molecular geometries were completely optimized either at the Hartree–Fock or DFT (B3LYP functional [17]) levels, the basis set being of 6-31G(d) quality. The gauge-including atomic orbitals (GIAO) [18,19] method was employed to calculate the absolute shielding constants (σ, in ppm) for TMS, DMDEOS and TEOS structure units. Subtraction gave the calculated chemical shift (δ, in ppm) of the structures relative to TMS. The basis sets of 6-31G(d) and 6-311 + G(2d,p) quality were used in the computation of the ^{29}Si SCF-NMR shifts.

3. NMR method-optimization of the DEPT pulse sequence

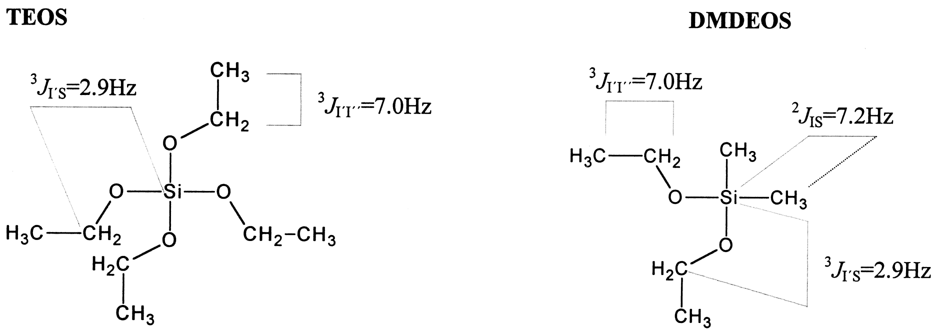
Although the DEPT pulse sequence is a well-known NMR technique [20–22], its parameters have to be adjusted for optimum performance. For that purpose, coherence evolution for the studied system should be analyzed. Standard DEPT pulse sequence consists of five pulses and three delays: 90°(^{1}H)-τ-180° (^{1}H), 90°(^{29}Si)-τ-θ°(^{1}H), 180(^{29}Si)-τ-acquisition (^{29}Si), broad-band (BB) decoupling (^{1}H). The final polarization state of a general multispin system I_nS immediately before acquisition and BB ^{1}H decoupling, expressed by the density matrix in the product operator representation, is [23]:

$$\sigma = nS_X \sin^{2n} \pi J\tau \sin\theta \cos^{n-1}\theta, \tag{1}$$

where S_X represents spin operator of heteronucleus (^{29}Si), J is heteronuclear coupling constant (^{1}H–^{29}Si), n is number of coupled proton spins and τ is close to 1/(2J). Listing only the sin terms, the evolution during the sequence can be expressed:

$$\begin{aligned} &nI_Z \xrightarrow{90_y(I)} nI_X \xrightarrow{\tau} n2I_XS_Z \sin\pi J\tau \xrightarrow{90_x(S)} n2I_XS_Y \\ &\times \sin\pi J\tau \xrightarrow{\tau} n2^nI_XS_{X,Y}(I_Z)^{n-1} \sin^n \pi J\tau \xrightarrow{\theta} n2^nS_{X,Y}(I_Z)^n \\ &\times \sin^n \pi J\tau \sin\theta\cos^{n-1}\theta \xrightarrow{\tau} nS_X \sin^{2n}\pi J\tau \\ &\times \sin\theta\cos^{n-1}\theta, \end{aligned}$$

where $S_{X,Y}$ means S_X or S_Y for n even or odd, respectively.



Scheme 1.

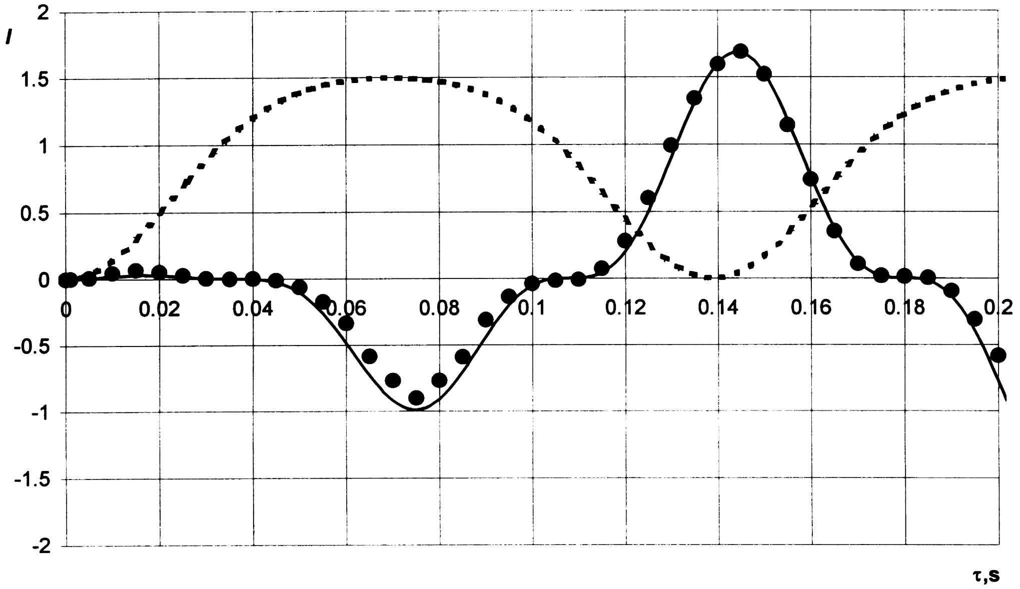


Fig. 1. Theoretical dependencies of signal intensities on polarization transfer time τ for $-Si(CH_3)_2-O-$ groups (dashed line) and TEOS (thick solid line) and experimental data obtained for TEOS (points ●).

From Eq. (1) it is clear that an optimum signal enhancement is achieved if τ is set to $1/(2J)$ and variable pulse θ to the following value:

$$\theta_{\mathrm{opt}} = \arcsin\left(\frac{1}{n}\right)^{(1/2)}. \qquad (2)$$

The problems in setting up optimum parameters follow directly from the difference of the spin systems of TEOS and DMDEOS. The latter is a complex $I_6I'_4I''_6S$ spin system consisting of six methyl protons with $^2J_{IS} = 7.2$ Hz, four ethoxy protons with $^3J_{I'S} = 2.9$ Hz and six methyl protons with $^3J_{I'I''} = 7.0$ Hz (cf. Scheme 1). For molecule of TEOS, the spin system is simpler, $I'_8I''_{12}S$, while the coupling constants are the same [24] (cf. Scheme 1). For optimum signal enhancement, the delays in DEPT experiment should be set equal to $1/(2J)$. However, the studied system contains at least two structure units with two different heteronuclear J couplings. During the first minutes of polycondensation, almost all ethoxy groups of DMDEOS are completely hydrolyzed, and the polarization transfer delay τ has to be adjusted to the value corresponding to the spin–spin interaction of methyl protons with silicon nuclei (coupling constant $^2J_{IS} = 7.2$ Hz). Some ethoxy groups of TEOS are also hydrolyzed, but complete hydrolysis is not probable, owing to low water content in the reaction mixture; at least one or two ethoxy groups are still present. For this case, the transfer delay τ should be set to the value corresponding to

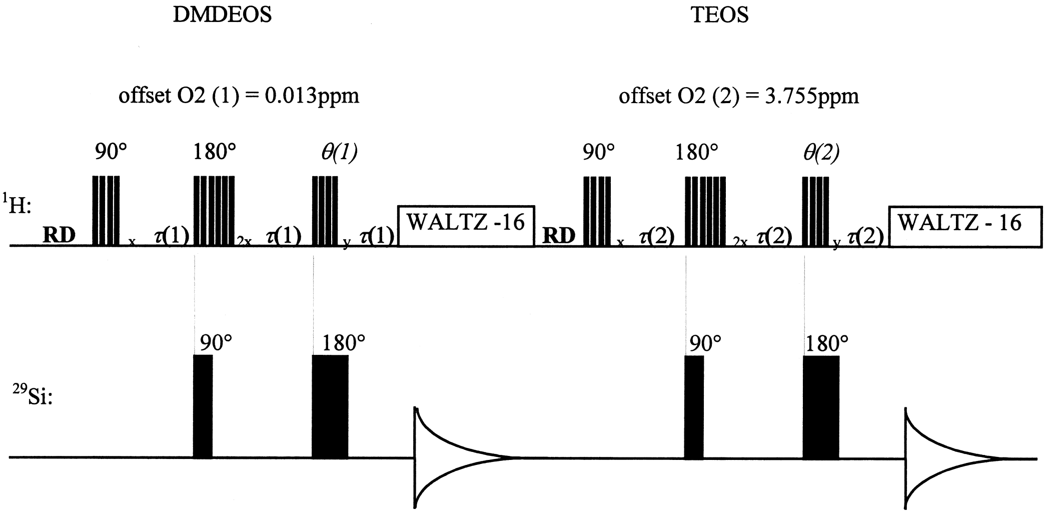


Fig. 2. DEPT pulse sequence with all ^1H selective pulses (DANTE). In the first part, e.g. methyl protons of DMDEOS units are selectively excited and polarization transfer time is equal $\tau(1) = 69.6$ ms ($^2J_{IS} = 7.2$ Hz), in the second part, protons of $-CH_2O-$ groups of TEOS are excited and polarization transfer time $\tau(2) = 172$ ms corresponds to the coupling constant $^3J_{IS} = 2.9$ Hz.

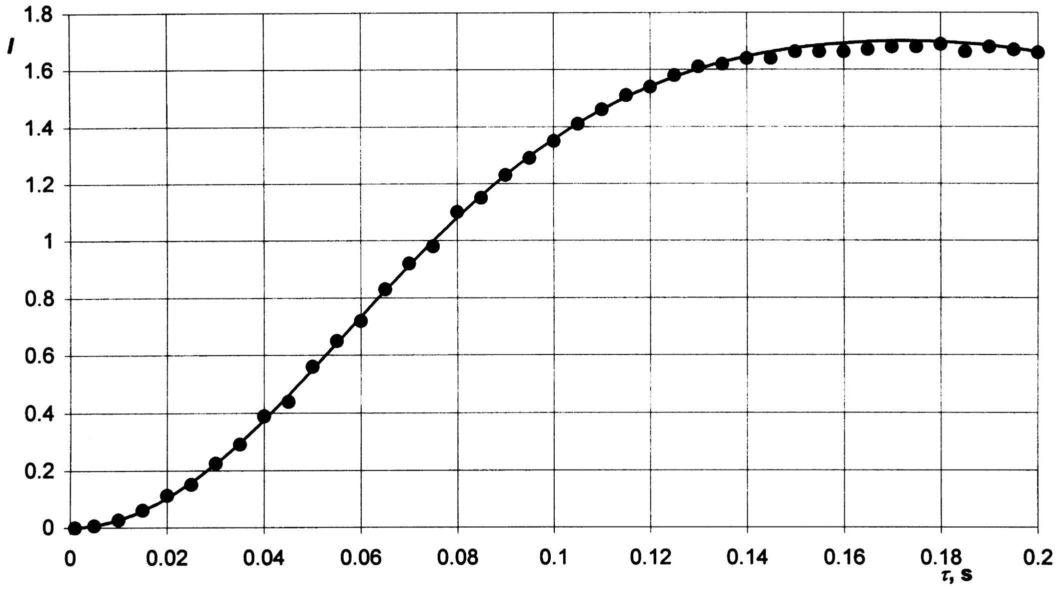


Fig. 3. The theoretical dependence (solid line) and experimental data (points ●) of signal intensity on polarization transfer time τ for $\mathrm{Si(O\mathbf{CH_2}CH_3)_4}$ groups of TEOS. Selective DEPT pulse sequence was used.

the heteronuclear coupling constant $^3J_{I'S} = 2.9$ Hz. From this it follows that to apply the standard DEPT pulse sequence for obtaining ^{29}Si NMR spectra of a mixture of those monomers, some intermediate value of τ delays should be used. However, as mentioned earlier, the calculated expression of the density matrix operator (1) is dominant only if the delays are close to the 1/(2*J*). If this condition is violated, additional observable terms appear due to incomplete defocusing during the second multiple-quantum period of the DEPT pulse sequence [25]. The spin density is then described by the following expression:

$$\sigma = nS_X \sin^2 \pi J\tau \sin \theta(\cos^2 \pi J\tau + \sin^2 \pi J\tau \cos \theta)^{n-1}, \quad (3)$$

provided all *I* spins are equivalent, i.e. the homonuclear spin coupling can be ignored. In our case for the TEOS units, however, also homonuclear couplings ($^2J_{I'I''} = 7.0$ Hz) must be taken into account as they are of the same order of magnitude as the heteronuclear long-range couplings, which are used for coherence transfer. As homonuclear couplings are active during the first two delays, the generalized form of Eq. (3) contains the multiplicative factor $\cos 2\pi J_{\mathrm{II}}\tau$ [26,27].

$$\sigma = \sum_n S_X \sin^2 \pi J_{I_nS}\tau \sin \theta \prod_{m\neq n} \cos 2\pi J_{I_nI_m}\tau(\cos^2 \pi J_{I_nS}\tau + \sin^2 \pi J_{I_nS}\tau \cos \theta)^{n-1}. \quad (4)$$

It follows from Eq. (4), that due to the strong dependence on the homonuclear coupling constant, optimum signal enhancement cannot be achieved by setting the delay τ according to the heteronuclear coupling constant. A similar expression of density matrix was derived for the case of spins with different heteronuclear couplings [25], e.g. in DMDEOS. However, the second heteronuclear coupling constant $^3J_{I'S} = 2.9$ Hz can be ignored, as nearly all ethoxy groups of DMDEOS monomer are hydrolyzed during the reaction. Thus, it is possible to assume that the second heteronuclear coupling constant does not affect signal enhancement of the units arising from DMDEOS during hydrolysis and condensation and the density operator (1) describes signal intensity.

In Fig. 1 the theoretical dependencies of signal intensity on the polarization transfer time τ are shown. The dependencies of $-\mathrm{Si(CH_3)_2O}-$ groups, formed during the fast hydrolysis of DMDEOS, and for TEOS were calculated according to Eqs. (1) and (4), respectively. Experimental data obtained for TEOS are in a good accord with the theoretical curve. These experimental data were obtained by applying standard DEPT pulse sequence with variable mixing pulse $\theta = 20.7°$. From this figure it follows that it is impossible to find the optimum polarization transfer time and retain high signal enhancement if the standard DEPT pulse sequence is applied to the mixture of TEOS and DMDEOS.

As a result of these findings, the DEPT pulse sequence was slightly modified. The experiment was divided into two parts as shown in Fig. 2. All pulses on protons were replaced by selective pulses and the DANTE method was used to generate selective ^{1}H pulses. The DANTE train consisted of 100 hard pulses (0.8 μs) spaced by 80 μs for a 90° ^{1}H pulse. Owing to the large difference in chemical shifts of signals, which were selectively, excited (ca. 740 Hz), the selectivity of the pulses could be restricted to a possible minimum. Thus, the length of the selective pulse was sufficiently short not to affect the coherence evolution considerably. In the first half of this experiment, only methyl protons of DMDEOS units are selectively excited. The delay $\tau(1) =$ 69.6 ms corresponds to the anti-phase coherence evolution

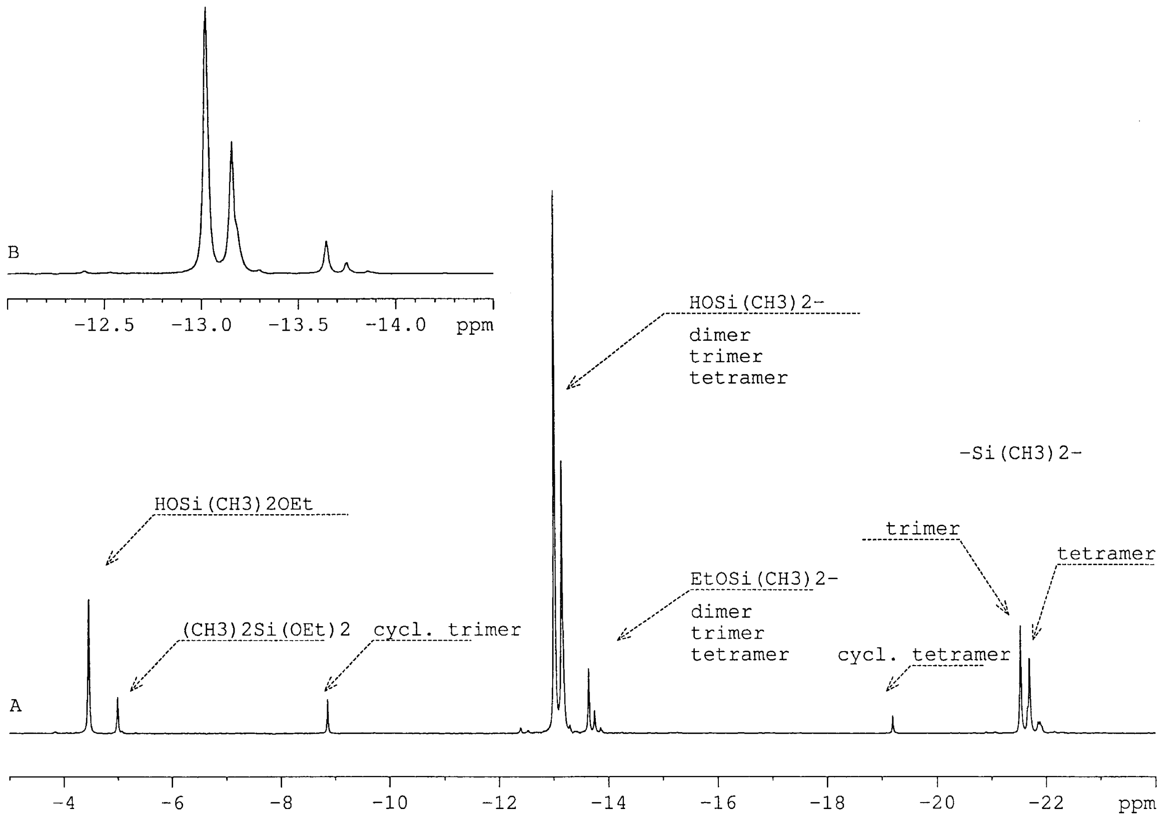


Fig. 4. ^{29}Si NMR spectrum (A) and its expanded part (B) of the DMDEOS reaction mixture after 30 min.

of the heteronuclear coupling constant $^{2}J_{IS} = 7.2$ Hz. Only signals arising from DMDEOS units are detected during the first acquisition. After relaxation delay, the second part of the sequence starts by changing frequency offset of ^{1}H radio-frequency field from methyl resonance (0.013 ppm) to ethoxy resonance (3.755 ppm). Next, the protons of $-CH_2-O-Si-$ groups of TEOS units are selectively excited. The delay $\tau(2) = 172$ ms correspond to the coupling constant of $^{3}J_{IS} = 2.9$ Hz. During the second acquisition, ^{29}Si signals corresponding to TEOS structure units are detected. Both FIDs can (but need not) be stored in the same buffer memory and, after finishing the experiment, processed into one spectrum where both the types of signals are presented. Owing to the short repetition delay (5 s) and alternative accumulation of both FIDs, the obtained data are only slightly time-averaged and distorted. The simplification of the coherence evolution sequence and, consequently, the simplification of the resulting density matrix operator is the main advantage of selective excitation of protons in the selective DEPT sequence. In this way, all passive I spins relate to S spin as well as to the active I_k spin as heterospins and multiplicative factor $\cos 2\pi J_{II}\tau$ in Eq. (4) vanishes. The optimum signal enhancement now depends only on the heteronuclear coupling constant. The theoretical dependence of signal intensity of TEOS on polarization transfer time and experimental data for selective DEPT pulse sequence are shown in Fig. 3 (cf. Fig. 1.) Maximum signal intensity is achieved at 172 ms, which correspond directly to the heteronuclear coupling constant $^{3}J_{IS} = 2.9$ Hz. Another advantage of this selective DEPT pulse sequence is the possibility of setting up the length of variable pulse directly for the measured spin subsystem according Eq. (2). In this case, the first variable pulse $\theta(1)$ had the length 24°, which corresponds to six methyl protons in DMDEOS units. The second pulse $\theta(2) = 30°$ was optimized for four ethoxy protons in arising TEOS units because hydrolysis and condensation of two ethoxy groups of TEOS units in later stages of the reaction are very probable. Now the intensity of signals can be standardized according to Eq. (1) and used for quantitative evaluation.

4. Results and discussion

4.1. Polycondensation of DMDEOS

Polycondensation of DMDEOS was studied mainly for simplification of signal assignment of ^{29}Si NMR spectra of the reaction mixture containing DMDEOS and TEOS. Polycondensation of TEOS under the same or similar reaction conditions was studied in our previous works [10,11] and is also described in the literature [3,4,6,12–14].

It is generally accepted that in alkoxysilanes, the increasing density of positive charge on silicon atom, which

Table 1
Comparison of calculated and experimental ^{29}Si NMR chemical shifts (ppm, TMS) of nonhydrolyzed dimer DMDEOS (1) EtO–Si*$(CH_3)_2$–O–Si*$(CH_3)_2$–OEt and partially hydrolyzed dimer DMDEOS (2) HO–Si*$(CH_3)_2$–O–Si*$(CH_3)_2$–OEt (calculated Mulliken charges on silicon atoms are shown in brackets)

		Ab initio method			Experimental data
		HF/6-31G(d)//HF/6-31G(d)	B3LYP/6-31G(d)//B3LYP/6-31G(d)	HF/6-311 + G(2d,p)//B3LYP/6-31G(d)	
1	Si (−OEt)	−10.0 (1.42)	−10.8 (0.98)	−13.8 (2.43)	−13.9
2	Si (−OEt)	−7.9 (1.42)	−8.5 (1.00)	−12.8 (2.30)	−13.9
	Si (−OH)	−6.7 (1.37)	−6.1 (0.96)	−10.6 (2.15)	−13.3

induces paramagnetic shielding, causes a “high-field” shift of its ^{29}Si NMR signals [6,24]. The signals of ^{29}Si in cyclic products of condensation, in contrast to linear ones, show a “low-field” shift because the cyclization reduces the –O–Si–O– valence angles and, consequently, the density of positive charge on silicon atom. For a similar reason, it is possible to differentiate between the ^{29}Si atoms in various linear oligomers up to the hexamer [6]. A similar relation is valid in many other cases because the changes in local charge density around the ^{29}Si nucleus are reflected mainly by the paramagnetic component of chemical shielding tensor, whereas the diamagnetic component mostly remains constant. However, this is not a rule and it is possible to find many deviations [24], especially in the range of chemical shifts from 20 to −20 ppm. Therefore, ab initio quantum-chemical calculations of ^{29}Si chemical shifts were used as an aid for assignment of some signals.

As hydrolysis of DMDEOS is very rapid, we expected the presence of two groups of signals (in the range from −13 to −14 ppm) corresponding to the end units containing hydroxy and ethoxy groups. These presumptions were in accord with experimental data as can be seen in Fig. 4. However, according to literature [12], signals in the range from −13.25 to −13.44 ppm correspond to dimers or ending units of linear oligomers, where ethoxy groups were not hydrolyzed. Then signals at −13.94 to −14.03 ppm would correspond to the end units, which contain hydroxy substituents. This contradicts the aforementioned rule of induction of paramagnetic shielding by increasing the density of positive charge on silicon atom. Owing to the fact that the effective electronegativity of oxygen atom is lower in the more ionic OH bond than in the ethoxy one, it is clear, that the substitution of ethoxy by hydroxy group leads to a decrease in the density of positive charge on silicon atom (in agreement with quantum chemical calculation; see Table 1), which should cause a low-field shift [6]. This presumption is quite valid for ^{29}Si NMR signals of monomers and oligomer products of hydrolysis of TEOS and TMOS [3,4,6,10–14]. ^{29}Si NMR signals of units containing hydroxy groups are a low-field shifted from signals of those containing ethoxy groups. Quantum chemical calculations of the ^{29}Si NMR chemical shifts indicate that the aforementioned rule is valid also in the case of DMDEOS. Calculated chemical shifts for two different structures of DMDEOS together with corresponding experimental data are given in Table 1. On the basis of these calculations and comparisons, we assigned signals at about −13.25 to −13.44 ppm to the end groups containing hydroxy groups, contrary to the data from the literature [12]. A good agreement of the calculated results with the experimental data, should be noted. This justifies utilization of chemical shift calculations as a useful tool for signal assignment. Complete ^{29}Si NMR signal assignment is presented in Table 2.

It should be also noted that in the region from −13.9 to −14.2 ppm, ^{13}C satellites, i.e. signals arising from splitting of central signal by ^{13}C–^{29}Si spin–spin interaction, appear. These ^{13}C satellites are apparent for the signal of cyclic tetramer where the coupling constant $^{1}J_{13C-29Si} = \pm 75.39$ Hz could be determined (see Fig. 5). It is in good agreement with the value of this coupling constant for DMDEOS reported in literature [24] ($^{1}J_{13C-29Si} = -73$ Hz).

Table 2
Chemical shifts (δ) of signals ^{29}Si of structure units relative to TMS

δ ppm	Structure unit [a]	
−4.76	HO–Si*– $(CH_3)_2$–OEt	D0
−5.31	$(CH_3)_2$–Si*– $(OEt)_2$	D0
−9.10	– (Si*$(CH_3)_2$–O)$_3$ cyclic trimer	D2-H
−13.25	HO–Si*$(CH_3)_2$–O–dimer	D1-H
−13.38	HO–Si*$(CH_3)_2$–O–trimer	D1-H
−13.41	HO–Si*$(CH_3)_2$–O–tetramer	D1-H
−13.44	HO–Si*$(CH_3)_2$–O– higher oligomers	D1-H
−13.94	EtO–Si*$(CH_3)_2$–O– dimer	D1-H
−14.03	EtO–Si*$(CH_3)_2$–O– trimer	D1-H
−19.44	– (Si*$(CH_3)_2$–O)$_4$ cyclic tetramer	D2-H
−21.76	HO–Si$(CH_3)_2$–O–Si*$(CH_3)_2$–O–Si$(CH_3)_2$–OH trimer	D2-H
−21.81	– (Si*$(CH_3)_2$–O)$_5$ cyclic pentamer	D2-H
−21.92	HO–Si$(CH_3)_2$–O–Si*$(CH_3)_2$–O– tetramer and higher oligomers	D2-H
−22.10	HO–Si$(CH_3)_2$–O–Si– $(CH_3)_2$–O–Si*$(CH_3)_2$–O– pentamer and higher oligomers	D2-H

[a] Si*: observed ^{29}Si.

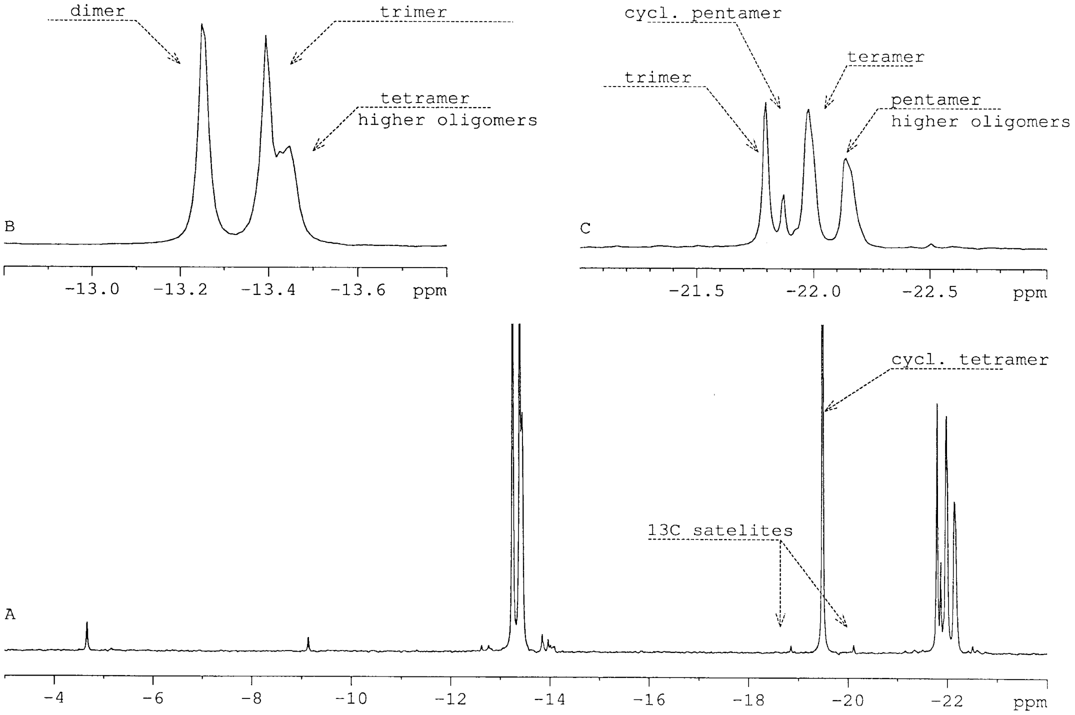


Fig. 5. ^{29}Si NMR spectrum (A) and its expanded part (B) of the DMDEOS reaction mixture after 2000 min.

4.2. Polycondensation of a DMDEOS–TEOS mixture

The presence of species originating from copolymerization of TEOS and DMDEOS considerably complicates the interpretation of ^{29}Si NMR spectra (cf. Figs. 6 and 7). It is impossible to definitely assign all ^{29}Si NMR signals to corresponding structure units. By applying the aforementioned semiempirical rule and with the help of ab initio calculations of chemical shifts, it is possible to carry out some assumptions and to assign regions of signals to groups of corresponding species. According to the literature data [1], copolymerization of the TEOS and DMDEOS units causes a low-field shift of ^{29}Si NMR signals of the TEOS and DMDEOS structure units. In the case of the low-field shift of signals of DMDEOS units, the changes in charge density on silicon atoms of the DMDEOS apparently affect not only the paramagnetic component of chemical shielding tensor but also the diamagnetic one, for which a high-field shift, due to the presence of TEOS unit in their close vicinity, would be expected. To be more sure in assigning the signals of formed oligomers, ab initio calculations of ^{29}Si NMR chemical shifts, which proved to be very valuable in the previous case, were performed. Quantum-chemical calculations do not allow an analysis of the problem of dia- and paramagnetic terms, as they are mere approximations based on a first-order perturbation approach. The results of the calculations using a large basis set for three structures of cyclic tetramers are shown in Fig. 8. We chose the cyclic tetramers for these calculations, as they can be a basis for formation of primary building units. In addition, cyclic tetramer of DMDEOS is unambiguously detected by the signal at −19.44 ppm. A tentative signal assignment to the corresponding species was made by comparing the experimental data with the calculated values using differences in ^{29}Si NMR shifts found for DMDEOS cyclic tetramers with various chemical structures. Although the calculated chemical shifts exhibit slight systematic deviations from the experimentally determined values, the low-field shifts of signals of DMDEOS units in rings containing TEOS unit is quite obvious. We assigned the ^{29}Si NMR signals in this region to DMDEOS and TEOS units in these structures. Thus, signals in the region from −16.0 to −19.2 ppm correspond to DMDEOS units, which are built in cyclic tetramers containing one to three TEOS units. These corresponding TEOS units resonate in the region from −93.4 to −94.6 ppm. Our suggestions are shown in Fig. 8. The values of chemical shift in brackets correspond to the signals detected in ^{29}Si NMR spectra. Complete signal assignment of copolymers is listed in Table 3. Signal assignments of homopolymers DMDEOS and TEOS are given in Table 2 and in the literature [6,10,14,28]. The signals ranging from −21.2 to −22.2 ppm correspond to the inner units of DMDEOS homopolymers or to longer sequences of these units. Three well-resolved signals in this region correspond to middle units of trimer, tetramer and pentamer (cf. Table 2). We assume that signals at ca. −21.2 ppm indicate longer sequences of DMDEOS units, the distance of which from a TEOS unit in oligomer chain is much larger because their chemical shifts are only slightly affected by copolymerization. Unresolved signals in the region from −19.5 to

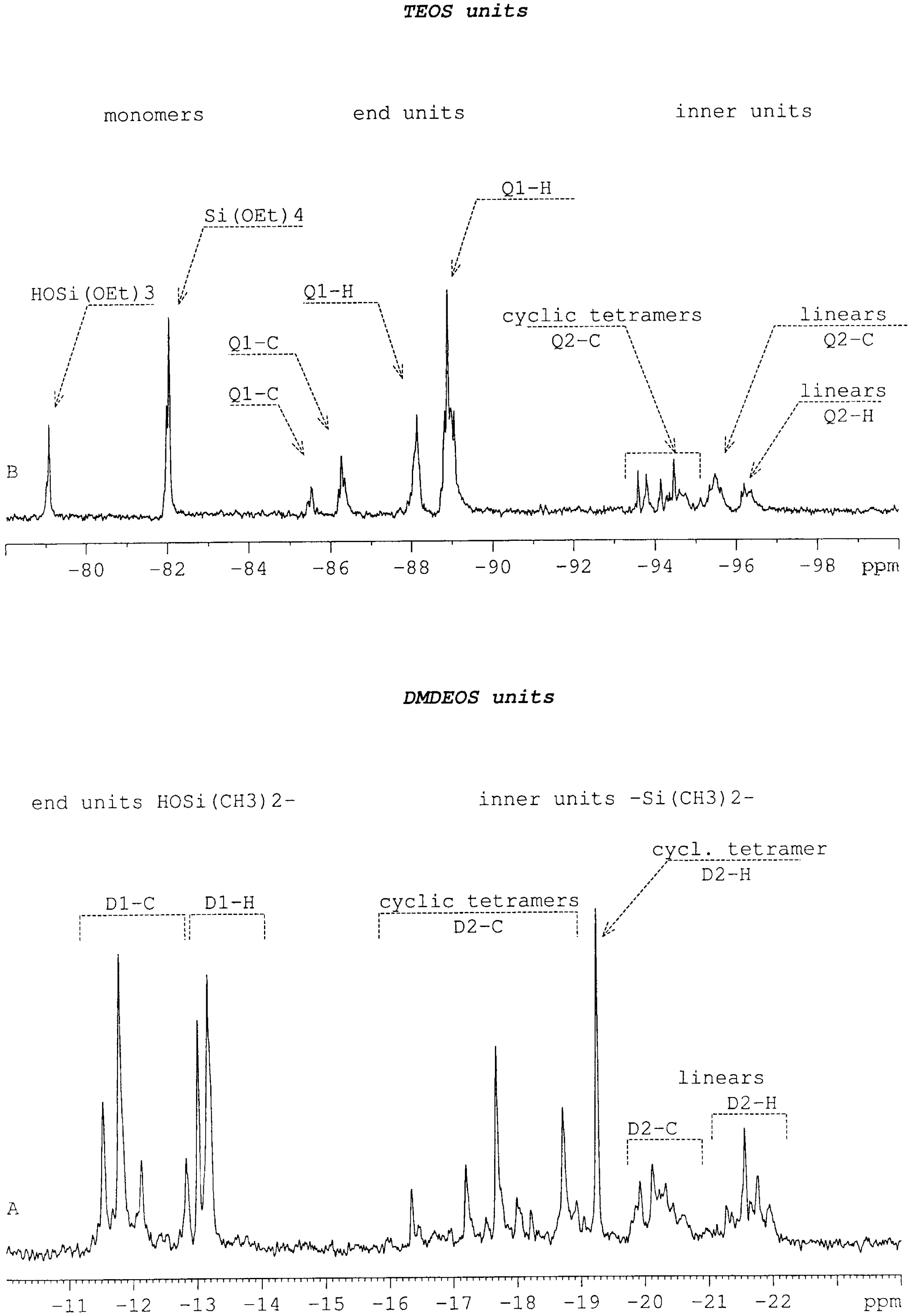


Fig. 6. ^{29}Si NMR spectrum of DMDEOS species (A) and TEOS species (B) of the DMDEOS + TEOS reaction mixture after 5300 min.

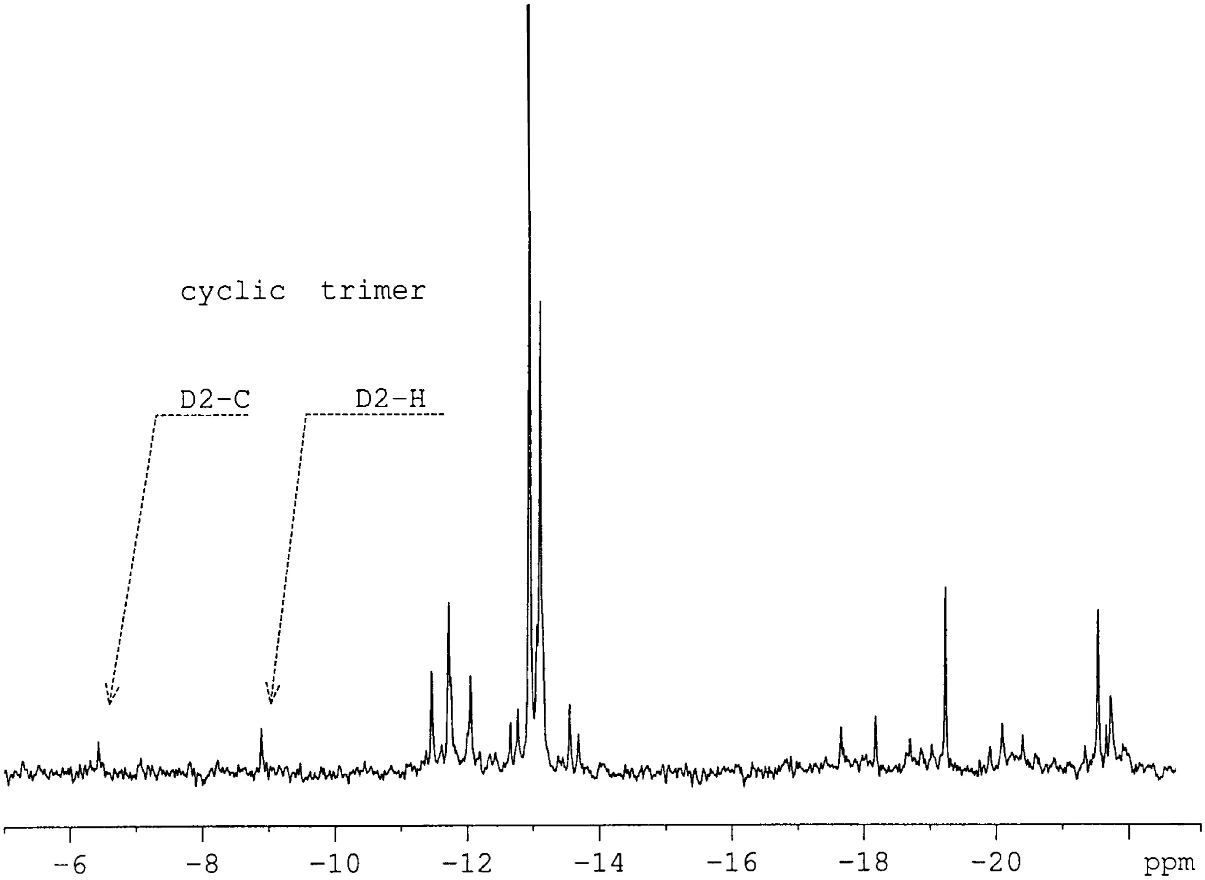


Fig. 7. ^{29}Si NMR spectrum of DMDEOS species of the DMDEOS + TEOS reaction mixture after 300 min.

−20.8 ppm indicate the presence of inner DMDEOS units as products of TEOS and DMDEOS copolymerization. These DMDEOS units are in close proximity with TEOS unit with chemical shift at ca. −95.0 to −96.0 ppm. Three signals at ca. −13 ppm indicate the end chain units of DMDEOS homopolymer or their longer sequences (D1H). The DMDEOS units of copolymers (D1C) that are very close to a TEOS unit are indicated by signals in the region from −11.2 to −12.5 ppm. Their position also reflects different extent of hydrolysis of TEOS structure units; however, an accurate assignment could not be performed. Differently hydrolyzed TEOS end units of copolymer are indicated by signals at about −85.2 and −86.4 ppm.

The earlier presented signal assignment made it possible to evaluate the reactivities of both monomers as well as arising products of self-condensation and copolymerization. The time dependence shown in Fig. 9 proves that the DMDEOS is highly reactive compared with the TEOS under the same conditions. Monomeric DMDEOS disappeared within 60 min while TEOS and its hydroxy derivates were found in the reaction mixture even after five days of reaction. High reactivity of DMDEOS is displayed by rapid formation and subsequent consumption of its dimers and short homopolymers during condensation as indicated by the time dependence of the signals of the corresponding end units (D1-H) (Fig. 9). In contrast, similar structure units of TEOS (Q1-H) arise much more slowly and their content in the reaction mixture is constant in later stages of the reaction. As follows also from Fig. 9, the process of copolymerization of TEOS with DMDEOS is little slower compared with self-condensation of DMDEOS. During the first steps of the reaction, when reaction mixture contains both TEOS and DMDEOS monomers (0–60 min), the dimers of $HO–Si(CH_3)_2–O–Si(OEt)_3$ and $HO–Si(CH_3)_2–O–Si–(OEt)_2–OH$ (D1C–Q1C) are the products of polycondensation. After consumption of the monomer DMDEOS, the dimer DMDEOS (D1H–D1H) becomes the most reactive component of the reaction mixture and reacting with monomer TEOS and also with the TEOS end unit of the dimer (D1C–Q1C). The resulting formation of tetramers (D1C–Q2C–D2C–D1C) can explain the decreasing content of end units Q1-C and the increase in units D1-C. From this also follows that the reactivity of TEOS unit grows considerably by its copolymerization with DMDEOS. The time dependencies presented in Fig. 10 also indicate that the arising copolymer is mainly formed by DMDEOS units. After five days of reaction, inner parts of the copolymers are composed of 60% of DMDEOS structure units (D2-C) and 40% of TEOS units (Q2-C). However, a much larger difference is observed in the composition of

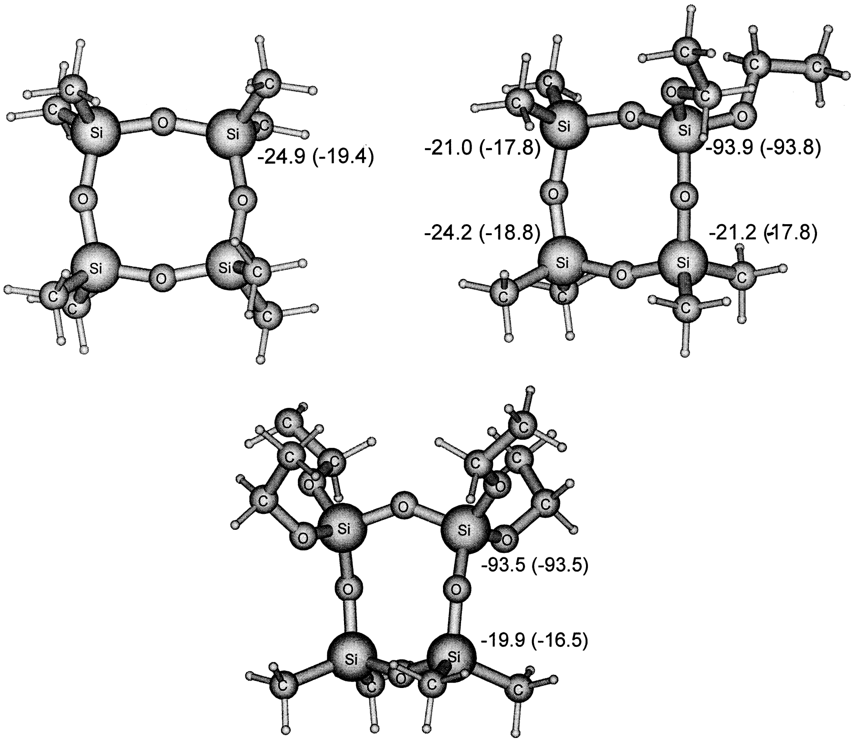


Fig. 8. Optimized geometries of three structures of DMDEOS cyclic tetramers calculated at the HF/6-31G(d) level. ^{29}Si NMR chemical shifts were calculated with the 6-311 + G(2d,p) basis set, values in brackets show experimental data for the signals in ^{29}Si NMR spectra assigned to corresponding Si atoms.

the ends of copolymer molecules. They are formed only by 14% of TEOS units (Q1-C), while the remaining 86% of end units are made by DMDEOS units (D1-C). This suggests that, due to higher functionality, TEOS end units (Q1-C) are preferred during subsequent condensation. From the knowledge of the content of inner and end chain units, it is possible to determine the number-average polymerization degree, $\overline{P}_n$, of copolymers and homopolymers of TEOS and DMDEOS. If cyclization reactions are not taken into account, the number-average polymerization degrees of copolymers are 7.8, 5.6 and 2.3 for the copolymer, and the corresponding DMDEOS and TEOS homopolymers, respectively. This shows that the copolymerization of DMDEOS with TEOS is more advantageous compared with the self-condensation of TEOS or DMDEOS. However, as the extent of cyclization reactions in alkoxysilane polycondensation is large, the aforementioned results have to be corrected. (The content of inner units of cyclic oligomers was not included into this calculation.) As we were not able to determine the content of cyclic units of TEOS (Q2-H), the number-average polymerization degree was recalculated only for the copolymer ($\overline{P}_n = 4.4$) and

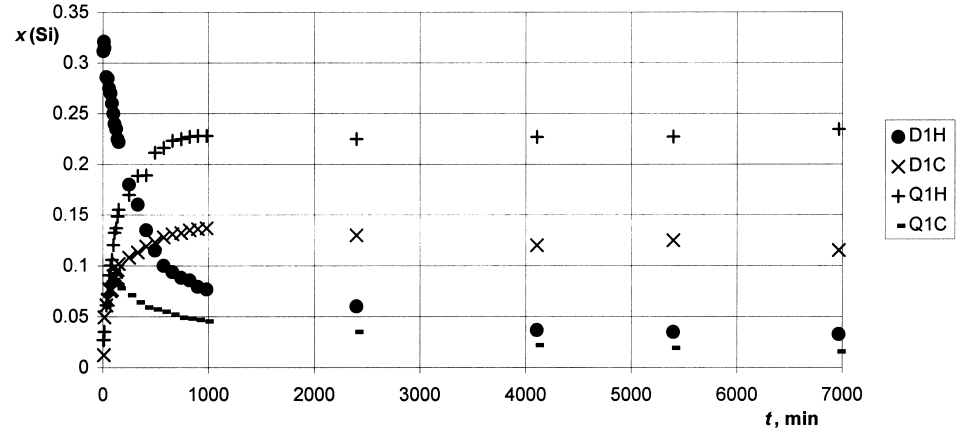
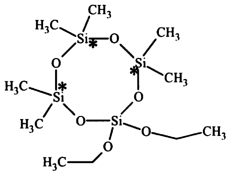
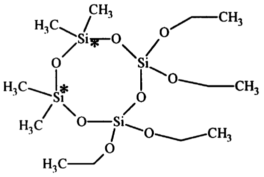
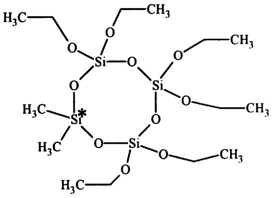
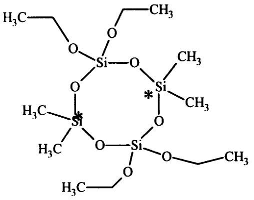


Fig. 9. Time dependencies of the relative concentration of DMDEOS end chain units of homopolymer D1H (●) and copolymer D1C (×) and TEOS end chain units of homopolymer Q1H (+) and copolymer Q1C (–).

Table 3
Chemical shifts (δ) of signals ^{29}Si of structure units relative to TMS

δ ppm	Structure unit[a]	
−6.62	–O–Si*(CH$_3$)$_2$–O–Si– (OEt)$_2$–O–Si*– (CH$_3$)$_2$– cyclic timer	D2-C
−11.72	HO–Si*(CH$_3$)$_2$–O–Si– (OEt)$_3$, HO–Si*(CH$_3$)$_2$–O–Si– (OEt)$_2$–OH	D1-C
−11.97	HO–Si*(CH$_3$)$_2$–O–Si– (OEt)$_2$–O–Si–,	D1-C
−12.32	HO–Si*(CH$_3$)$_2$–O–Si(CH$_3$)$_2$–Si– (OEt)$_2$–O–Si–,	D1-C
−13.02	…etc.…	D1-C
−16.54		D2-C
−17.39		D2-C
−17.86		D2-C
−18.19		D2-C
−18.85 −19.9 to −20.9	HO–Si(CH$_3$)$_2$–O–Si*(CH$_3$)$_2$–Si– (OEt)$_2$–O–Si– –O–Si(CH$_3$)$_2$–O–Si*(CH$_3$)$_2$–Si– (OEt)$_2$–O–Si– – (OEt)$_2$–O–Si–O–Si*(CH$_3$)$_2$–Si– (OEt)$_2$–O…etc.…	D2-C
−85.55 to −85.81	HO– (OEt)$_2$–O–Si*–O–Si(CH$_3$)$_2$–OH, HO– (OEt)$_2$–O–Si*–O–Si(CH$_3$)$_2$–O–	Q1-C
−86.29 to −86.75	(OEt)$_3$–O–Si*–O–Si(CH$_3$)$_2$–OH, (OEt)$_3$–O–Si*–O–Si(CH$_3$)$_2$–O–	Q1-C
−93.79 −93.99 −94.34 −94.65 −94.80	Cyclic tetramers Observed silicon atom originating from TEOS	Q2-C
−95.2 to −96.1	–O–Si(CH$_3$)$_2$–O– (OEt)$_2$–O–Si*–O–Si(CH$_3$)$_2$–OH –O–Si(CH$_3$)$_2$–O– (OEt)$_2$–O–Si*–O–Si(CH$_3$)$_2$–O– –O–Si(CH$_3$)$_2$–O– (OEt)$_2$–O–Si*–O– Si– (OEt)$_2$–O…etc.…	Q2-C

[a] Si*: observed ^{29}Si.

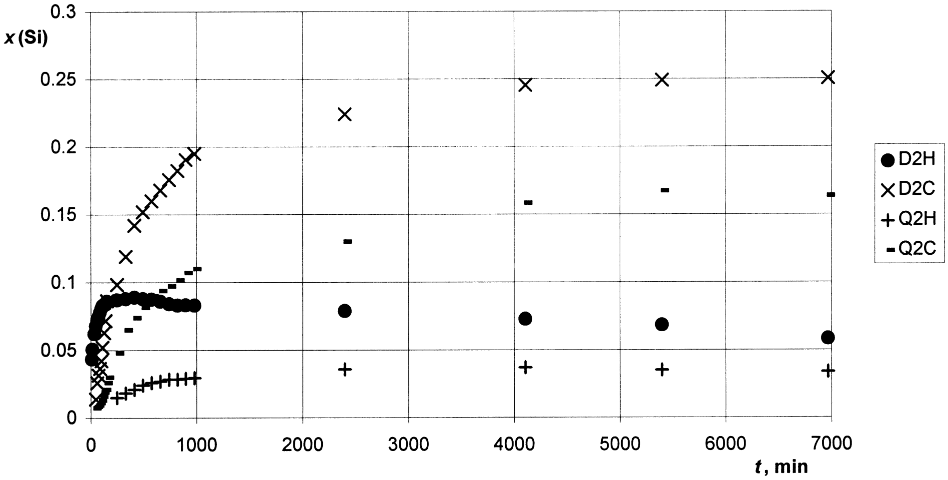


Fig. 10. Time dependencies of the relative concentration of DMDEOS inner chain units of homopolymer D2H (●) and copolymer D2C (×) and TEOS end chain units of homopolymer Q2H (+) and copolymer Q2C (–).

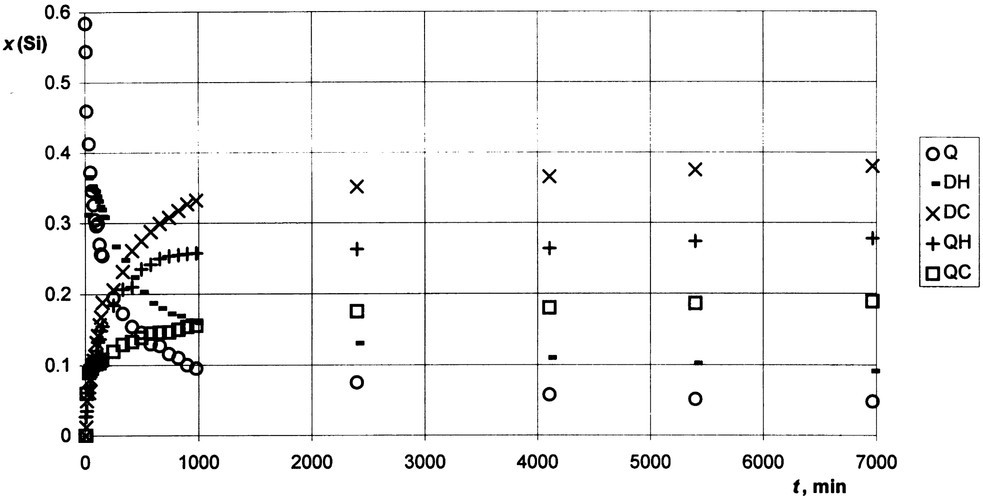


Fig. 11. Time dependencies of the relative concentration of TEOS and DMDEOS structure units in homopolymers, copolymers and monomers: (○) TEOS monomer, (–) DMDEOS homopolymer, (×) DMDEOS copolymer, (+) TEOS homopolymer and (□) TEOS copolymer.

DMDEOS homopolymer ($\overline{P}_n = 3.8$). The time dependence of relative concentrations of TEOS and DMDEOS structure units in homopolymers, copolymers and monomers DMDEOS a TEOS (D1 + D2, Q1 + Q2) is shown in Fig. 11. It is clear that, due to higher reactivity, the first step of reaction of TEOS and DMDEOS mixture is a very fast self-condensation of DMDEOS during which mainly dimers and short oligomers are formed. At the same time, a little slower copolymerization of TEOS a DMDEOS occurs. Owing to copolymerization of DMDEOS homopolymers with copolymers, 80% of DMDEOS units are built in the copolymers and only 20% of DMDEOS units form homopolymers after five days of reaction. At the same time, 9% of TEOS units are not yet condensed, 54% of TEOS units form dimers and a small amount of short oligomers due to self-condensation, and only 37% of TEOS units are included in the copolymers. The copolymers are thus formed by 30% of TEOS and 70% of DMDEOS structure units. As the ends of copolymer chains are formed mainly by DMDEOS units, they could copolymerize with TEOS units in the later reaction stages. However, it cannot be excluded and it seems to be very probable that during the final stages of reaction small domains composed only from TEOS structure units can arise. It is also necessary to note that, cyclization is a significant process during polycondensation of alkoxysilanes, and after five days of reaction, almost 30% of both the types of structure units (DMDEOS and TEOS) are involved in cyclization products (trimers, tetramers and pentamers). We assume that these cyclic products can form small building units of the arising gel, the small oligomer chains containing only TEOS being possible links. This mechanism is apparently complicated by a cleavage of cyclic trimers at the later reaction phases. This interesting phenomenon has not been observed with TEOS [28,29]. The presence of small amount of DMDEOS monomer indicates hydrolysis of siloxane bonds and cleavage of some oligomers. This fact can play a very important role in the formation of small building units and finally of siloxane materials giving the possibility of forming the most advantageous building units and arrangements of the material.

5. Conclusion

Using a modified DEPT sequence (the original experiment was divided into two parts and all pulses on protons were replaced by selective pulses) enabled us to obtain quantitative ^{29}Si NMR spectra of the reaction mixture of TEOS and DMDEOS during their polycondensation.

Quantum chemical ab initio calculation of structures and ^{29}Si NMR chemical shifts of some products proved very useful and helpful for signal assignment. Our calculations show that the ab initio calculations of chemical shifts at the Hartree–Fock or DFT levels provide results, which are close to experimental data even for relatively large molecules and large atoms such as silicon. From the trends of ^{29}Si NMR chemical shifts, it was possible to make signal assignment with adequate certainty. Although the assignment of every individual signal to the corresponding structure unit is not yet unambiguous, a semiquantitative analysis of relations in the reaction mixture of TEOS and DMDEOS could be done. From this analysis it follows that although the reactivity of the DMDEOS monomer is much higher in comparison with TEOS, the arising gel is not strictly phase separated and copolymerization of both monomers occurs. In the first stages of the process, the resulting oligomers are composed of 70% of DMDEOS structure units. From this it follows that at the final stages of polycondensation, we can assume the formation of domains of TEOS structure units. As the cyclization is a significant process in polycondensation of alkoxysilanes, we suggest, that these TEOS domains or oligomers can act as the linking units between the cyclic oligomers.

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