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Od Redakcji

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Copolymerization of functional cyclotrisiloxanes — a reactivity comparison^{**)}

Summary — Kinetics of controlled simultaneous copolymerization of hexamethylcyclotrisiloxane (D_3) with functional cyclotrisiloxanes was studied using *n*-BuLi in THF as initiator. Trifunctional $(MeXSiO)_3$ (X_3), where X = vinyl, trifluoropropyl or chloropropyl group, and monofunctional monomers $[(Me_2SiO)_2MeXSiO]$ (D_2X), where X = cyanopropyl or *n*-octyl group, were used as monomers. Reactivity ratios for each pair of comonomers were determined and the possibility of synthesis of gradient copolymers by this method is discussed.

Key words: cyclosiloxanes, polysiloxanes, gradient copolymers, anionic ring opening polymerization, reactivity ratio.

KOPOLIMERYZACJA FUNKCYJNYCH CYKLOTRISILOKSANÓW — PORÓWNANIE REAKTYWNOŚCI

Streszczenie — Zbadano kinetykę kontrolowanej kopolimeryzacji jednoczesnej heksametylocyklotrisiloksanu (D_3) z funkcyjnymi cyklotrisiloksanami inicjowanej *n*-BuLi w THF. Jako cyklotrisiloksany funkcyjne zastosowano trójfunkcyjne $(MeXSiO)_3$ (X_3), gdzie X — grupy winylowa, trifluoropropylowa albo chloropropylowa [odpowiednio $(D^{Vi})_3$, $(D^{PrF_3})_3$ lub $(D^{PrCl})_3$] oraz monofunkcyjne $[(Me_2SiO)_2MeXSiO]$ (D_2X), gdzie X — grupy cyjanopropylowa lub *n*-oktylowa (odpowiednio D_2D^{PrCN} i D_2D^{Oct}) (rys. 1–4). Wyznaczono współczynniki reaktywności komonomerów we wspomnianych układach i omówiono możliwość syntezy na tej drodze kopolimerów gradientowych. Metodą DSC scharakteryzowano przemiany cieplne badanych produktów (rys. 5). Przedys-

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kutowano też wyniki obliczeń kwantowo-chemicznych i zagadnienia stabilności kompleksów jonów Li^+ z niektórymi badanymi monomerami cyklotrisiloksanowymi (rys. 6 i 7).

Słowa kluczowe: cyklosiloksany, polisiloksany, kopolimery gradientowe, anionowa polimeryzacja z otwarciem pierścienia, współczynniki reaktywności.

Polysiloxanes show several features which make them unique among the other polymers. This is a result of the fact that the siloxane chain exhibits unusual static flexibility, in terms of a huge number of available conformations, and dynamic flexibility, related to the low barriers of the conformational change. This feature in combination with low intermolecular forces are responsible for exceptionally low glass transition temperatures, low melting points and small viscosity changes with temperature of dialkyl-substituted polysiloxanes [1].

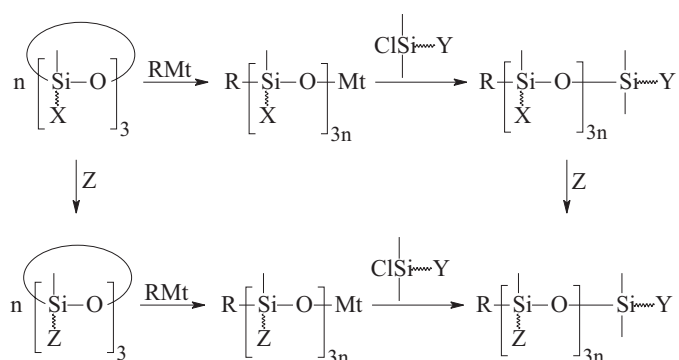
On the other hand, polar Si-O backbone and nonpolar organic pendant groups impose amphiphilic character upon polysiloxanes which, together with exceptional chain flexibility, results in their unique surface properties, such as low surface tension, fast diffusion to the interface, facile conformational adaptation to the lowest free energy state of the system, *etc.* [2, 3]. These features make polysiloxanes very valuable materials for a wide range of applications and provoke a continuing interest in new polysiloxanes with improved properties.

Our goal was to examine the possibility to obtain gradient siloxane copolymers, in which the instantaneous composition varies continuously along the chain but a composition of all chains is homogeneous. Such polymers are expected to combine unique properties of polysiloxanes with the advantageous features related to a gradient composition of the backbone. Latest reports suggest that the physical properties of gradient copolymers differ considerably from those of block and random copolymers [4–8]. The main effects are related to the differences in morphology and local dynamics, which manifest themselves in a broad spectrum of relaxation times of segmental motions of the chains. These copolymers, having a controlled variable composition along the backbone, are a new promising class of materials with tunable microstructures and physical properties. They can potentially be used as polymer blend compatibilizers, surfactants, and environment-sensitive materials, for example, materials for vibration and noise dampening [5].

The synthesis of gradient copolymers requires controlled polymerization techniques which assure well defined molecular weight (M_n), its polydispersity (M_w/M_n), and the functional group distribution [4, 5]. Anionic ring-opening copolymerization of cyclotrisiloxanes is the only method so far, that makes possible the synthesis of functional polysiloxanes with a precise control of all above-mentioned structural features of the polymer. The silanolate active propagation centres are stable under vacuum or in an inert gas atmosphere and the side reactions involving polymer chain, such as back-biting and chain transfer, may be avoided or largely suppressed,

which makes the polymerization system close to an ideal living one [9].

If the desired functional groups at silicon atom are labile under basic conditions, for example, $-\text{H}$, $-\text{CH}_2\text{Cl}$, and $-\text{CH}_2\text{C}(\text{O})\text{OR}$, the monomers with stable precursor groups can be used. Such precursor groups may be later transformed to the desired functions by reactions on the polymer (Scheme A).



Scheme A. Modification of functional groups in the anionic ring opening polymerization (AROP) of cyclotrisiloxanes

The most common precursor group used in the anionic polymerization of cyclosiloxanes is the vinyl group [10]; chloropropyl and hydrogen groups were also used with caution [11, 12].

Gradient copolymers can be obtained by the controlled simultaneous copolymerization of two monomers. The resulting chain microstructure depends on the reactivities of both monomers (*i.e.*, how fast they build into the chain) and may be modified by changing the initial monomer ratio. Gradient copolymers are formed when monomer reactivity ratios are different but not much. If they are too different, tapered, quasi-block copolymers are created in which only the very narrow gradient link between the homogeneous blocks occurs. The alternative is the semi-batch method, which enforces the gradient composition along the chain using virtually any pair of monomers by adding one monomer continuously to the polymerization mixture.

EXPERIMENTAL

Materials

Solvents

Tetrahydrofuran (THF, POCH) was purified by refluxing and distilling from sodium and kept under

vacuum over Na/K alloy in an ampoule fitted with a Rotaflo stopcock. *n*-Heptane, undecane, and dichloromethane (POCH) were purified by standard methods (*n*-heptane and undecane were distilled from CaH₂). Acetone and methanol (POCH, analytical grade) were used as received. Trimethylchlorosilane [(CH₃)₃SiCl] (ABCR), was purified by distillation.

Initiators

n-Butyllithium (2.5 M solution in *n*-heptane, Aldrich) was analyzed by the standard method [13] and used as received.

Monomers

Hexamethylcyclotrisiloxane (D₃, Dow Corning) was kept melted over CaH₂ in an ampoule equipped with a teflon stopcock for several days and distilled under vacuum. Other monomers, prepared according to the described methods (see Scheme B and C) were purified in the same way. The purity of monomers checked by GC was higher than 99 %.

Synthesis of copolysiloxanes – general procedure

Gradient and block copolymers of functional cyclotrisiloxane (X₃ or D₂X) with hexamethylcyclotrisiloxane were synthesized according to the procedure described in [14].

Kinetics of the copolymerization – general procedure

Known amounts of monomers – D₃ and X₃ or D₂X – were distilled on a high vacuum line to a glass reactor. Then THF was distilled under vacuum into the reactor to obtain a 50 wt. % solution of the monomers in THF. The reactor was filled with dry argon, fitted with a magnetic stirrer and thermostated at 22 °C. Then undecane (a reference standard for gas chromatography, GC) and *n*-BuLi in *n*-hexane solution were introduced. The mixture was stirred at 22 °C, and the samples were withdrawn at regular time intervals by a Hamilton syringe through the stopcock under a positive pressure of nitrogen. The samples were quenched by injection to a mixture of Me₃SiCl/Et₃N, centrifuged and analysed by GC. The polymerization was quenched by introducing the same mixture when total conversion of monomers exceeded 95 % and the reaction mixture was stirred by another 1 h. Solvent and excess of Me₃SiCl were evaporated under vacuum. In the case of (D^{Pr}E₃)₃ copolymerization the polymer was precipitated from a acetone/methanol mixture. The polymer was dissolved in CH₂Cl₂ and precipitated three times with methanol. The resulted copolymer was heated for several hours under high vacuum to remove the volatile fraction and subjected to ¹H and ²⁹Si NMR and SEC analysis. The final yield of polymer was *ca.* 80 %.

Analyses

Gas chromatography

GC analyses were performed on Hewlett Packard 6890 apparatus with catarometer detector fitted with 30 m capillary HP-1 column. Carrier gas was helium. Temperature program: from 60 °C to 240 °C, heating rate 10 deg/min, injector temperature 250 °C.

NMR studies

¹H and ²⁹Si NMR spectra were taken with a Bruker 500 MHz or Bruker AC200 MHz spectrometer using CDCl₃ as solvent. Quantitative integration was achieved using the inverse gated decoupling technique in the presence of Cr(acac)₃. A pulse delay of 15 s was usually applied and a typical pulse length was 15 μs. Conditions of analysis were the same as in [14].

Size exclusion chromatography

SEC analyses were performed on an LDC Analytical refractoMonitor IV instrument working with RI detector and equipped with two columns SDV 8 × 300, 5 μm and 104 Å of porosity and SDV 8 × 300, 5 μm and 100 Å of porosity. Toluene was used as eluent at a flow rate of 0.7 mL/min. Molecular weights were calculated relative to polystyrene standards.

Differential scanning calorimetry measurements

Phase transitions of the copolymers were studied by DSC technique using a DuPont 2000 thermal analysis system. Thermograms were taken for samples quenched rapidly from the melt upon heating at a rate of 10 deg/min. The transition temperatures were taken as corresponding to the maximum of the enthalpic peak.

Simulation procedure

Kinetics of copolymerization of X₃ + D₃ was simulated by numerical solving of the differential kinetic equations using the analogous procedure to that described in [14]. Kinetic equations used for simulation are presented in the further text, Eqs. (1) and (2).

Quantum chemical calculations

All calculations were performed with the Gaussian 03 program [15]. Equilibrium geometries were optimized with the B3LYP/6-31G(d) method. All stationary points were verified by frequency analysis. Thermal corrections to the enthalpy and entropy at 298 K were scaled by 0.98. Final electronic energies were calculated at the B3LYP/6-311+G(2d,p) level. Orbital interaction analysis was performed using the Natural Bond Orbital theory

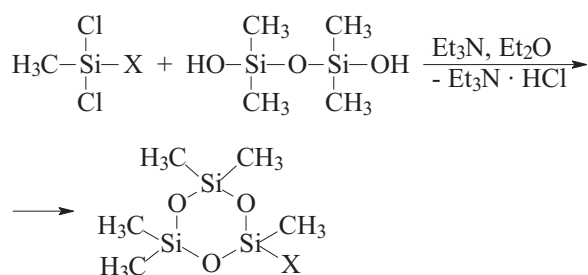
[16]. Calculations were performed for the gas phase conditions.

RESULTS AND DISCUSSION

We present here the results of kinetic studies of copolymerization of hexamethylcyclotrisiloxane (D_3) with several functional cyclotrisiloxanes having vinyl, trifluoropropyl, chloropropyl, octyl and cyanopropyl groups at Si atom. Each of these functional groups is important in the silicone technology. The vinyl and chloropropyl groups are versatile precursors often used for further functionalisation of polysiloxanes [10, 17–19]. Fluoroalkyl groups improve resistance to fuel, oils and hydrocarbon solvents as well as antifouling properties of silicones [2, 20]. Cyanoalkyl silicones show high solvent resistance. They can be used as dielectric materials, antifoam and antistatic agents [17], solid electrochemical devices [21] and as ligands binding metals to form magnetic fluids [22]. Polysiloxanes with long alkyl side chains such as octyl, show liquid crystalline morphologies [23]. In our study we used trifunctional cyclic monomers, $(MeXSiO)_3$, where X = vinyl, trifluoropropyl and chloropropyl groups, and monofunctional cyclic monomers, $[(Me_2SiO)_2MeXSiO]$, where X = cyanopropyl or n -octyl group. These monomers will be further denoted as X_3 and D_2X , respectively.

Synthesis of functional cyclotrisiloxanes

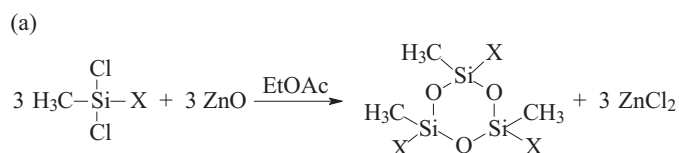
Monofunctional cyclotrisiloxanes D_2X were obtained by heterofunctional condensation of functional dichlorosilanes with tetramethyldisiloxanediol (Scheme B) [24].



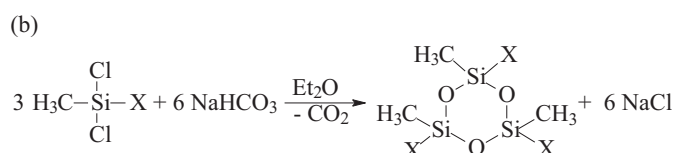
$X = -(CH_2)_3CN, -CH=CH_2, -n-C_8H_{17}$

Scheme B. Synthesis of monofunctional cyclotrisiloxanes (D_2D^X)

Trifunctional cyclotrisiloxanes X_3 were prepared in anhydrous coupling of the corresponding dichlorosilanes [Scheme C(a) or C(b)]. The route C(a) is a commonly used procedure for making these monomers [25]. However it gives poor yields when X = chloropropyl and in this case the method C(b) appeared to be more effective [11].



$X = -CH=CH_2, -(CH_2)_3CN$

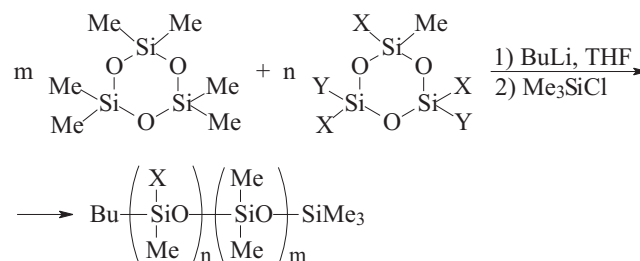


$X = -(CH_2)_3Cl$

Scheme C. Synthesis of trifunctional cyclotrisiloxanes (D^X_3)

Kinetics of copolymerization

Kinetics of the simultaneous copolymerization of a mixture of D_3 with functional cyclotrisiloxanes in THF using n -BuLi as the initiator (Scheme D) was followed by GC, measuring conversions of the monomers. The main objective was to determine the reactivity ratios of all



$X = -CH=CH_2, -(CH_2)_2CF_3, -(CH_2)_3CN, n-C_8H_{17}$

$Y = X$ or Me

Scheme D. Synthesis of siloxane copolymers by simultaneous copolymerization of D_3 with functional cyclotrisiloxanes

comonomer pairs. The knowledge of reactivity ratio values is important to predict the copolymer composition at given initial concentrations of monomers [26]. Examples of kinetic runs for various copolymerization systems are shown in Figures 1–4.

Copolymerization of D_3 with 2,4,6-trivinyl-2,4,6-trimethylcyclotrisiloxane (D^{Vi}_3) is reported in detail elsewhere [27, 28]. The D_3 with 2,4,6-tris(3,3,3-trifluoropropyl)-2,4,6-trimethylcyclotrisiloxane ($D^{PrF_3}_3$) copolymerization system was also described recently [29]. Therefore, these systems are briefly mentioned here only for comparison with three others [$D_3 + (D^{PrCl})_3$, $D_3 + D_2D^{PrCN}$ and $D_3 + D_2D^{Oct}$].

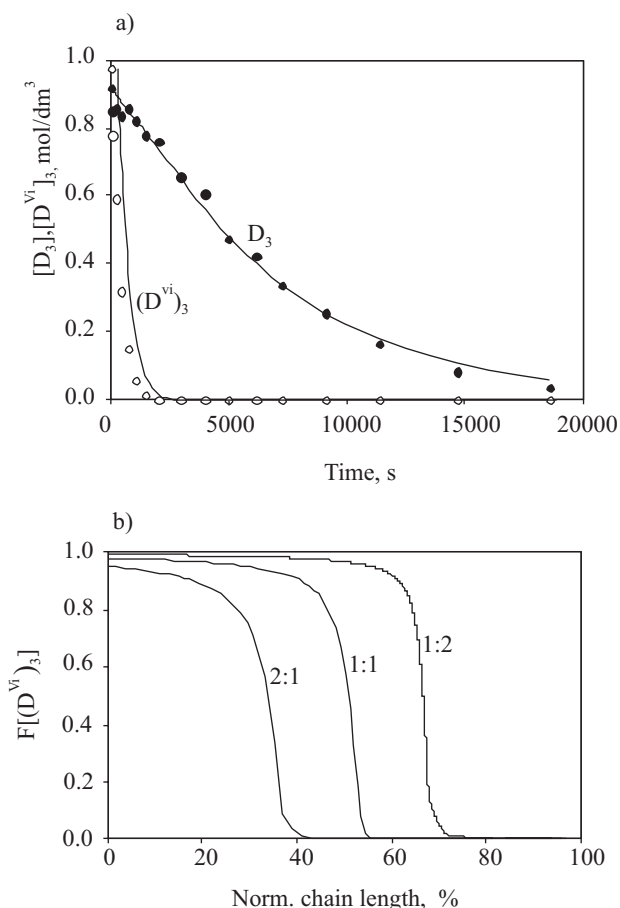


Fig. 1. (a) Kinetics of simultaneous copolymerization of D_3 + $(D^{VI})_3$ (1:1), initiated by BuLi in THF: $[D_3]_0 = [(D^{VI})_3]_0 = 1.0 \text{ mol} \cdot \text{kg}^{-1}$, $[\text{BuLi}]_0 = 0.056 \text{ mol} \cdot \text{kg}^{-1}$, $T = 22 \text{ }^\circ\text{C}$; (b) instantaneous chain composition $F[(D^{VI})_3]$ at various initial proportions of monomers (1:2, 1:1 and 2:1)

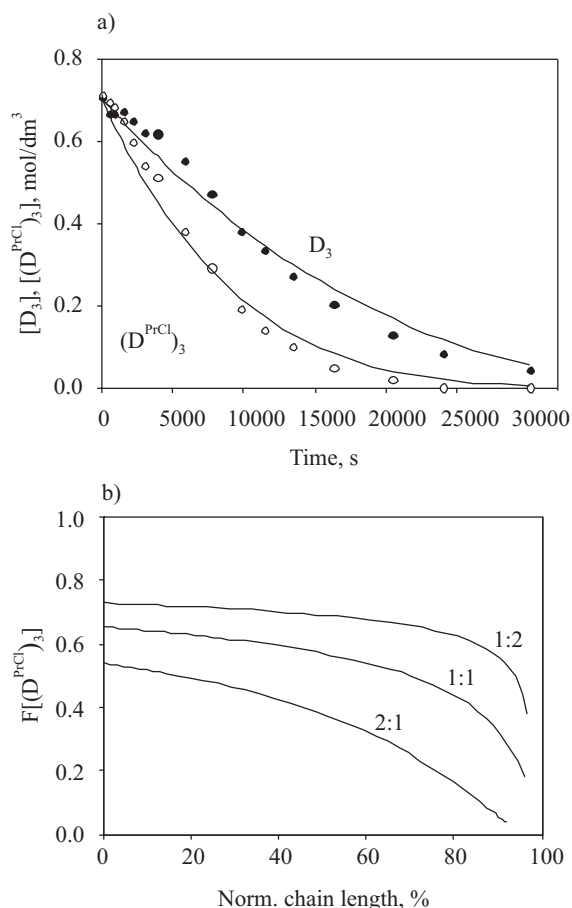


Fig. 2. (a) Kinetics of simultaneous copolymerization of D_3 + $(D^{\text{PrCl}})_3$ (1:1), initiated by BuLi in THF: $[D_3]_0 = [(D^{\text{PrCl}})_3]_0 = 0.8 \text{ mol} \cdot \text{kg}^{-1}$, $[\text{BuLi}]_0 = 0.035 \text{ mol} \cdot \text{kg}^{-1}$, $T = 22 \text{ }^\circ\text{C}$; (b) instantaneous chain composition $F[(D^{\text{PrCl}})_3]$ at various initial proportions of monomers (1:2, 1:1 and 2:1)

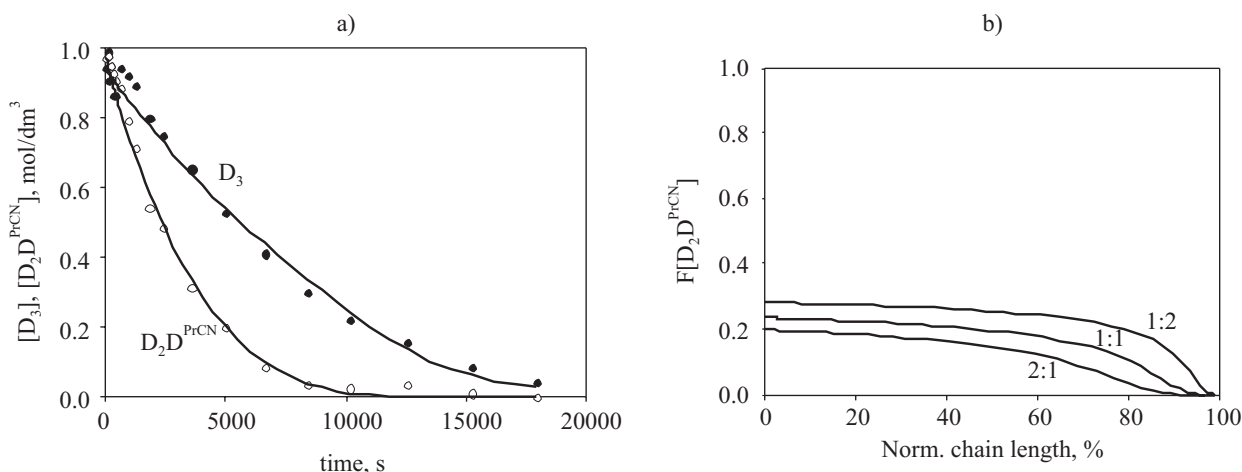


Fig. 3. (a) Kinetics of simultaneous copolymerization of D_3 + D_2D^{PrCN} (1:1), initiated by BuLi in THF: $[D_3]_0 = [D_2D^{\text{PrCN}}]_0 = 1.0 \text{ mol} \cdot \text{kg}^{-1}$, $[\text{BuLi}]_0 = 0.037 \text{ mol} \cdot \text{kg}^{-1}$, $T = 22 \text{ }^\circ\text{C}$; (b) instantaneous chain composition $F[D_2D^{\text{PrCN}}]$ at various initial proportions of monomers (1:2, 1:1 and 2:1)

The kinetics of monomer conversion was analysed by a computer simulation using well-known Mayo-Lewis equations (1), where D^* and X^* are the silanolate active centres $\sim\text{Me}_2\text{SiOLi}$ and $\sim\text{MeXSILi}$, respectively. The ap-

parent rate constants of the elementary propagation reactions were determined by a numerical integration of differential equations (1a)–(1c) based on the data of the monomers conversion with time. Initiation was assumed

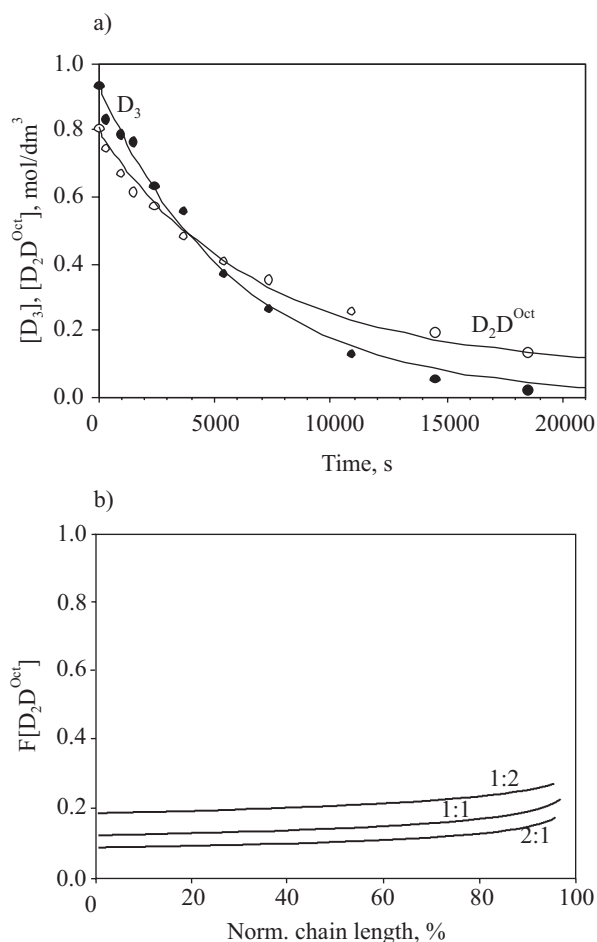


Fig. 4. (a) Kinetics of simultaneous copolymerization of $D_3 + D_2D^{Oct}$ (2:1), initiated by BuLi in THF: $[D_3]_0 = [D_2D^{Oct}]_0 = 1.0 \text{ mol} \cdot \text{kg}^{-1}$, $[BuLi]_0 = 0.037 \text{ mol} \cdot \text{kg}^{-1}$, $T = 22 \text{ }^\circ\text{C}$; (b) instantaneous chain composition $F[D_2D^{Oct}]$ at various initial proportions of monomers (1:2, 1:1 and 2:1)

instantaneous. Reactivity ratios were calculated as $r_D = k_{DD}/k_{DX}$, $r_X = k_{XX}/k_{XD}$, where k_{ij} are the apparent rate constants. The rate constants of homopolymerizations of all monomers used were independently determined by kinetic experiments.

$$-\frac{d[D_3]}{dt} = k_{DD}[D^*][D_3] + k_{XD}[X^*][D_3] \quad (1a)$$

$$-\frac{d[X_3]}{dt} = k_{DX}[D^*][X_3] + k_{XX}[X^*][X_3] \quad (1b)$$

$$\frac{d[D^*]}{dt} = -\frac{d[X^*]}{dt} = k_{XD}[X^*][D_3] - k_{DX}[D^*][X_3] \quad (1c)$$

It should be mentioned that the Mayo-Lewis scheme for anionic ROP of cyclosiloxanes (and for many other anionic systems) is only an approximation. Silanolates are known to exist in equilibrium with higher aggregates which are assumed inactive. This leads to fractional orders with respect to the initiator [30]. Thus, the values reported here should be considered as the apparent reactivity ratios, which in fact may be not constant (as the apparent rate constants may vary depending on the con-

centrations of monomers and initiator), but still may be useful for predicting the polymer composition in the limited range of concentrations of the monomers and initiator.

Reactivity ratios for the $D_3 + (D^{Vi})_3$ copolymerization system determined for a series of kinetic runs at various concentrations of monomers and initiator are $r_D = 0.011$, $r_V = 49.3$ [28]. Reactivity ratios for the $D_3 + (D^{PrF_3})_3$ copolymerization system were reported in the previous paper [29]. The reactivity ratios estimated by simulation and by the based on experimental results Kelen-Tüdös method [31] for all systems are collected in Table 1. The results given by both methods agree reasonably well. There is no systematic change in the apparent rate constants in the range of concentrations studied. Thus, the error arises mainly from the imprecise measurements of concentrations by gas chromatography and curve fitting.

Table 1. Reactivity ratios in the $D_3 + X_3 (D_2X)$ copolymerization systems initiated by BuLi in THF

| | $(D^{Vi})_3$ | $(D^{PrF_3})_3$ | $(D^{PrCl})_3$ | D_2D^{PrCN} | D_2D^{Oct} |
|---------------------|---------------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|
| Computer simulation | $r_{D_3} = 0.011$ $r_{X_3} = 49.3$ | $r_{D_3} = 0.10$ $r_{X_3} = 51.8$ | $r_{D_3} = 0.25$ $r_{X_3} = 1.36$ | $r_{D_3} = 0.19$ $r_{X_3} = 1.80$ | $r_{D_3} = 1.4$ $r_{X_3} = 0.67$ |
| Kelen-Tüdös method | $r_{D_3} = 0.19$ $r_{X_3} = 63.8$ | $r_{D_3} = 0.12$ $r_{X_3} = 38.0$ | $r_{D_3} = 0.21$ $r_{X_3} = 1.22$ | $r_{D_3} = 0.21$ $r_{X_3} = 1.93$ | $r_{D_3} = 1.46$ $r_{X_3} = 0.64$ |

$(D^{Vi})_3$ and $(D^{PrF_3})_3$ react so rapidly that only ca. 15–20 % of D_3 (depending on the initial proportions of monomers) is incorporated into the chain before more reactive monomers are totally consumed. The remaining D_3 forms a dimethylsiloxane block thereafter. It is possible to manipulate the functional group distribution to some extent by altering the X_3/D_3 initial ratio. However, in all cases the tapered block copolymers are obtained, consisting of the two almost homogeneous blocks joined with a short segment of gradient composition (see Fig. 1).

The difference in reactivity between D_3 and $(D^{PrCl})_3$, D_2D^{PrCN} and D_2D^{Oct} is small. The monomers with electron-withdrawing groups (PrCl and PrCN) are slightly more reactive than D_3 while the monomer containing *n*-octyl group is less reactive due to the steric reasons. The small reactivity difference is reflected in the chain composition which changes gradually from the chain beginning to the end. It has to be noted that when D_2X comonomer is used, the instantaneous fraction of X units in the chain cannot exceed 1/3 (see Fig. 3b, 4b).

Prediction of copolymer composition

Instantaneous compositions of copolymers calculated from the kinetic runs at $D_3/X_3(D_2X) = 2:1$, 1:1 and 1:2 ratio are shown in Fig. 1b–4b. The curves were generated using Equation (2).

$$F_x = \frac{r_x \cdot f_x^2 + f_x f_D}{r_x f_x^2 + f_x f_D + r_D f_D^2} \quad (2)$$

where: r_i — the reactivity ratios, F_i and f_i — instantaneous copolymer and comonomer feed fractions, respectively.

The comonomer fractions were taken from simulations.

In the case of monomers which reactivity ratios are very different, such as $D_3 + (D^{Vi})_3$ or $D_3 + (D^{PrF_3})_3$, the tapered blocky copolymers are obtained with a short gradient fragment in the middle of a polymer chain. To obtain polymers with more disperse gradient distribution, the semi-batch method has to be used which involves continuous addition of the more reactive monomer to the polymerization mixture [29].

Copolymers were characterized by SEC, 1H and ^{29}Si NMR spectroscopy and also DSC.

^{29}Si NMR spectroscopy is a convenient tool for the cumulative sequence analysis in copolymer chains. Assuming no chain scrambling (redistribution), only the following pentad sequences are allowed in the kinetically controlled process:

D-centered — DDDDD, DDDDX, DDDXX, XDDDX

X-centered — XXXXX, XXXXD, XXXDD, DXXXX

where: D = Me₂SiO, X = MeXSiO unit.

If the signals of pentad sequences are well separated, as it is the case for copolymers with vinylmethylsiloxane units, the sequence analysis can provide important information about the chain microstructure [14]. In most cases, however, the signals of different sequences overlap and the quantitative analysis of sequence distribution is impossible [29].

DSC analysis reflects significant differences in chain mobility of gradient copolymers compared to homopolymers and to block copolymers. Glass transitions as well as crystallization/melting points of both components are affected [4]. T_g of PDMS homopolymer is -129 to -127 °C

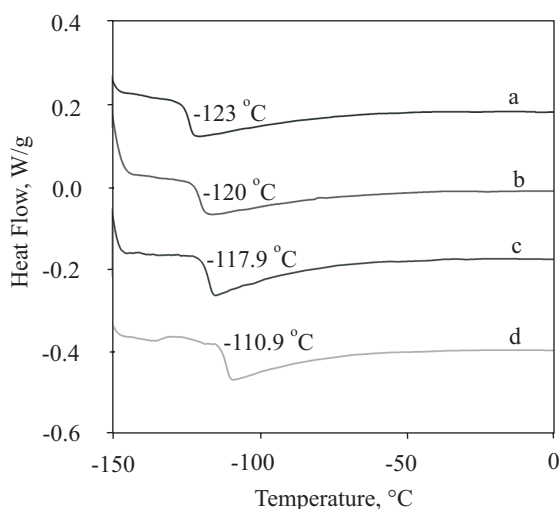


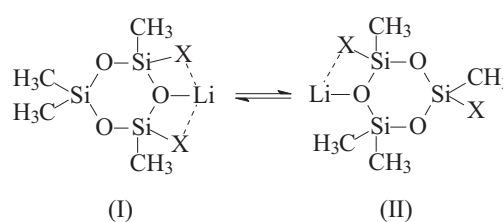
Fig. 5. DSC thermograms of copolymers prepared in the simultaneous copolymerization of D_3 with D_2D^{Oct} ; $D_3:D_2D^{Oct}$ proportions: a) 2:1, b) 1:1, c) 1:2, d) homopolymer D_2D^{Oct}

[1]. PDMS homopolymer of $M_n > 5000$ shows also a characteristic crystallization band at ca. 88 °C (depending on the cooling/heating rate) and two sharp endothermic peaks at -48 °C and -36 °C, corresponding to the melting [32]. In $D_3/(D^{Vi})_3$ and $D_3/(D^{PrF_3})_3$ gradient copolymers these melting transitions are preserved due to the presence of the pure PDMS block in the copolymer [28, 29]. In copolymers of D_3 with $(D^{PrCl})_3$, D_2D^{PrCN} and D_2D^{Oct} crystallization is completely suppressed due to the “true” gradient chain microstructure [33]. These copolymers show a single glass transition located in between of the T_g 's of both corresponding homopolymers. The glass transition temperature of a gradient copolymer shifts continuously depending on the monomer proportions in the copolymer [33]. Comparison of DSC thermograms for D_3/D_2D^{Oct} copolymers with different monomer proportions is presented in Fig. 5.

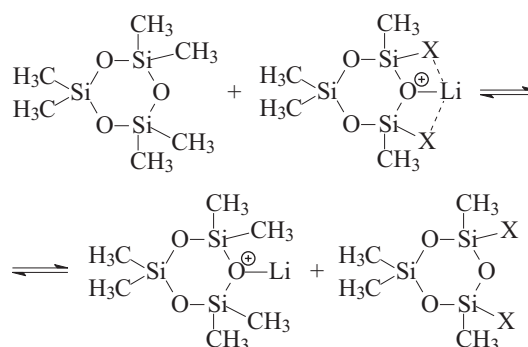
Quantum-chemical calculations

To explain the high reactivity of the trivinyl- and tris-trifluoropropyl-substituted cyclotrisiloxanes we have performed quantum-mechanical DFT calculations of the interaction of lithium cation with the corresponding cyclotrisiloxanes, D_3 , difunctional cyclotrisiloxanes (DX_2), namely 2,4-divinyltetramethylcyclotrisiloxane $D(D^{Vi})_2$ and 2,4-bis(3,3,3-trifluoropropyl)-tetramethylcyclotrisiloxane $D(D^{PrF_3})_2$ (Schemes E and F).

Structures I (Scheme E) are more thermodynamically stable than II by $\Delta G^{298} = 3.9$ and 4.1 kcal/mol for $X = Vi$ and $X = PrF_3$, respectively. Gibbs free energy for the Li^+ exchange between D_3 and D^{PrF_3} has been found to be even larger, 9.2 kcal/mol and for the analogous exchange



Scheme E. Exchange of the Li^+ cation between two nonequivalent oxygen atoms in $D(D^X)_2$



Scheme F. Exchange of the Li^+ cation between D_3 and $D(D^X)_2$

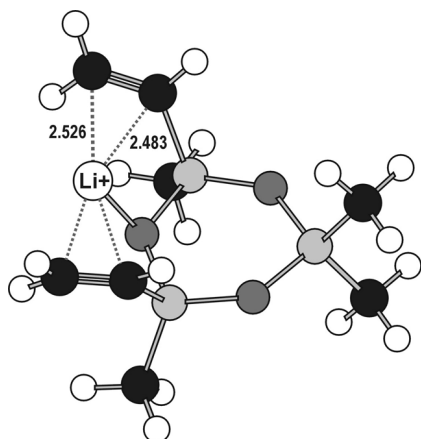


Fig. 6. B3LYP/6-31G* geometrical structure of Li^+ -*cis*-2,4-divinyltetramethylcyclotrisiloxane complex; distances from vinyl carbons to lithium are given in Å

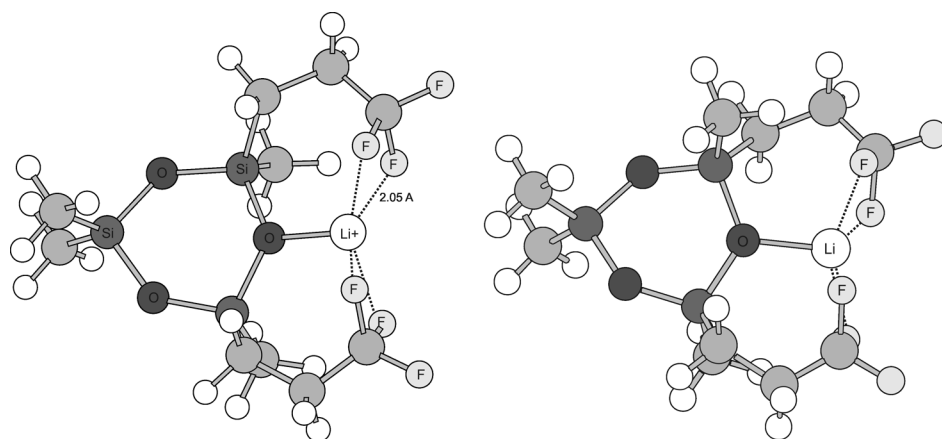


Fig. 7. B3LYP/6-31G* geometrical structures of the complexes of Li^+ with (a) *cis*-2,4-bis(3,3,3-trifluoropropyl)tetramethylcyclotrisiloxane; (b) *trans*-bis(3,3,3-trifluoropropyl)tetramethylcyclotrisiloxane

between D_3 and $\text{D}(\text{D}^{\text{PrF}_3})_2$, $\Delta G^{298} = 14.5$ kcal/mol. Thus, stabilization of lithium cation in the gas phase provided by the vicinal functional group is *ca.* 4.5 kcal/mol and 7.2 kcal/mol per one vinyl and trifluoropropyl group, respectively. This extra stabilization provided by vinyl groups is due to the $\pi(\text{C}=\text{C}) \rightarrow \sigma(\text{Li}^+)$ electron-donating interactions, as supported by the Natural Bond Orbital (NBO) analysis. This interaction is the most effective when two vinyl groups at adjacent silicon atoms are in *cis* position to each other (Fig. 6). Thus, *cis*- $(\text{D}^{\text{Vi}})_3$ is predicted to be more reactive than *trans*- $(\text{D}^{\text{Vi}})_3$.

Stabilization by trifluoropropyl groups is due to the $\text{p}(\text{F}) \rightarrow \sigma(\text{Li}^+)$ electron-donating interactions, according to the NBO analysis. The interaction in bis(trifluoropropyl)cyclotrisiloxanes is approximately equally effective for *cis* and *trans* regioisomers (Fig. 7). Thus, both stereoisomers are expected to exhibit similar reactivity.

Analogous interaction of metal cations with the phenyl rings was found to be responsible for different regioselectivity of ring opening of 2,2-diphenyltetramethylcyclotrisiloxane by lithium and potassium silanates [34].

Higher reactivity of vinylsiloxanes and trifluoropropylsiloxanes was attributed to the inductive effect of electron-withdrawing groups which make silicon more

electrophilic and therefore more susceptible to nucleophilic attack [35, 36]. Mulliken atomic charge analysis does not support this explanation. The charge on Si in $(\text{D}^{\text{Vi}})_3$ is +0.977 e while that in D_3 is +1.020 e. Upon attachment of lithium cation, the charge on the adjacent Si atom bound to vinyl increases to +1.112 e while that on Si substituted by two methyl groups increases to +1.150 e. Similar conclusions can be drawn from the charge distribution analysis in $(\text{D}^{\text{PrF}_3})_3$. Although atomic charge is not a quantum observable and different theoretical methods give different values, it may be concluded that the inductive effect is not the main factor responsible for the high reactivity of both cyclotrisiloxanes.

The values of apparent rate constants decrease in order $k_{\text{XX}} > k_{\text{DX}} > k_{\text{DD}} > k_{\text{XD}}$. Thus, D_3 and $(\text{D}^{\text{PrF}_3})_3$ add preferentially to both active chain ends, D^* and X^* . Quantum-chemical

calculations suggest that the enhanced reactivity of these monomers may result from their specific interactions with the active centres, in particular with the counter-ion. Such interactions affect the local composition of the feed in the vicinity of active centres and, consequently, distort the values of reactivity ratios calculated from the nominal composition of the feed. Such interactions have been suggested before to explain kinetic features of the anionic copolymerization of some olefins [37].

The interaction of the both monomers with lithium cation is expected to enhance its reactivity for two reasons. First, the charge transfer from silicon to lithium cation should increase the acidity of silicon atoms. Indeed, Mulliken atomic charge analysis shows that upon attachment of the lithium cation, the charge on the adjacent Si atoms bound to vinyl and trifluoropropyl groups increases by 0.14 e and 0.08 e, respectively. Second, the interaction of Li^+ with oxygen weakens the Si-O bonds in the oxonium center of the complex II (Scheme E). The Si-O bond lengths in the oxonium center increase upon attachment of Li^+ by 0.05 Å and 0.06 Å in $\text{D}(\text{D}^{\text{Vi}})_2$ and $\text{D}(\text{D}^{\text{PrF}_3})_2$, respectively.

Obviously, the discussed effect is less prominent in monosubstituted cyclotrisiloxanes, $\text{D}_2\text{D}^{\text{Vi}}$ and $\text{D}_2\text{D}^{\text{PrF}_3}$. $\text{D}_2\text{D}^{\text{Vi}}$ is more reactive than D_3 but considerably less reac-

tive than $(D^{Vi})_3$ [28]. The reactivities of the remaining monomers studied, $(D^{PrCl})_3$, D_2D^{PrCN} and D_2D^{Oct} , may be explained by the inductive and steric effects of the substituents. Electron-withdrawing chloropropyl and cyanopropyl groups are predicted to activate the cyclosiloxane towards the nucleophilic attack. This effect cannot be strong, as the electrophilic moiety, Cl or CN, is remote from the silicon atom, separated by the $(CH_2)_3$ linker. Moreover, these moieties are also unable to strongly interact with a counter-ion. In the case of octyl group the steric effect dominates, which reduces the reactivity of the monomer.

CONCLUSIONS

Anionic ring opening copolymerization of cyclotrisiloxanes is a convenient route to well-defined siloxane copolymers having gradient distribution of pendant groups along the chain. Simultaneous copolymerization of cyclotrisiloxanes leads to gradient copolymers provided the reactivity ratios of both comonomers are not very different. This situation occurs in the case of the systems D_3 and $(D^{PrCl})_3$, D_2D^{PrCN} or D_2D^{Oct} , where the differences in reactivity are small. Gradient siloxane copolymers containing these functional groups were obtained by simultaneous copolymerization of above-mentioned monomers. In $D_3 + (D^{Vi})_3$ and $D_3 + (D^{PrF_3})_3$ copolymerization systems the functional comonomers are much more reactive than D_3 and the copolymers of blocky structure with only short gradient segment between the blocks can be obtained.

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