

Terpolymerization of Cyclosiloxanes with Various Substituents at the Silicon Atoms

I. Yu. Ruskol^{a,*}, A. R. Dolotko^a, V. V. Kireev^a, A. K. Shestakova^b,
E. I. Alekseeva^b, V. Yu. Khudoleeva^a, and S. R. Nanush'yan^b

^a Mendeleev University of Chemical Technology, Miusskaya pl. 9, Moscow, 125047 Russia

^b State Research Center of the Russian Federation—State Research Institute of Chemistry and Technology of Organoelement Compounds, sh. Entuziastov 38, Moscow, 105118 Russia

*e-mail: ruskol_i@mail.ru

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Abstract—With the use of ²⁹Si NMR spectroscopy, gas–liquid chromatography, viscometry, refractometry, and gel permeation chromatography, the process of copolymer formation during anionic copolymerization of octamethylcyclotetrasiloxane, 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane, and 1,3,5-trimethyl-1,3,5-triphenylcyclotrisiloxane in the presence of the molecular-weight regulators hexamethyldisiloxane or trimethylsilanol has been studied. It has been shown that anionic copolymerization of the above cyclosiloxanes proceeds in two stages. At the first stage, poly(methylphenylmethylvinyl)siloxane with a structure varying from block to random is formed, and, at the second stage, octamethylcyclotetrasiloxane enters into the reaction to yield a random copolymer of a desired composition via chain transfer reactions. Under conditions of anionic copolymerization, hexamethyldisiloxane is inefficient as a chain-terminating agent owing to its low reactivity, whereas trimethylsilanol participates in copolymerization and controls the molecular weight of the copolymer through the reaction of proton–cation exchange with the propagating macroanion.

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Copolymerization of cyclosiloxanes with various organic substituents is widely used to obtain high-molecular polysiloxanes, particularly, polyorganosiloxanes containing vinyl and phenyl groups [1, 2].

Control over the molecular weights of the formed copolymers is commonly accomplished with the use of monofunctional compounds, for example, trimethylchlorosilane, hexamethyldisiloxane (HMDS), or trimethylsilanol (TMS).

In this paper, the results of the copolymerization of three cyclosiloxanes—octamethylcyclotetrasiloxane (D₄), 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane (V₄), and 1,3,5-trimethyl-1,3,5-triphenylcyclotrisiloxane (A₃)—in the presence of HMDS or TMS and the anionic initiator α,ω -bis(tetramethylammoniumpolydimethyl) siloxanolate (TMAS) are presented.

The main goal of this study was to determine how the character of the copolymer chain formation depends on the type of substituent in the cyclosiloxanes and the used molecular-weight regulators (HMDS or TMS).

Note that copolymerization of the three different cyclosiloxanes is poorly known [3]. The main data on these processes are given in the patent literature.

EXPERIMENTAL

Reagents

In experiments, octamethylcyclotetrasiloxane (244 FLUID, Dow Corning); 1,3,5-trimethyl-1,3,5-triphenylcyclotrisiloxane (OOO Khimprodukt, specifications 6-02-1-143-86); 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane (Q-12287, Dow Corning); and hexamethyldisiloxane, trimethylsilanol, and α,ω -bis(tetramethylammoniumpolydimethyl) siloxanolate (OOO PENTA-91) were used. None of the cyclosiloxanes was subjected to further purification except A₃, which was recrystallized from hexane. According to the GLC data, recrystallized A₃ contains 99.18% of the main compound (40.60% cis isomer and 58.58% trans isomer) and has a *T_m* value ranging from 40 to 60°C. The commercial solvents hexane and toluene (analytical grade, Komponent) and acetic acid (reagent grade, Laboratornaya Tekhnika) were used without further purification.

Copolymerization

Into a three-neck flask equipped with a stirrer, a thermometer, and a reflux, A₃ (27.2 g, 0.067 mol), D₄ (22.2 g, 0.075 mol), V₄ (34.4 g, 0.1 mol), and HMDS (8.1 g, 0.05 mol) or TMS (9 g, 0.1 mol) were charged.

Table 1. Compositions of the low-molecular-weight products of copolymerization of A₃, D₄, and V₄ in the presence of HMDS at various reaction times

Reaction time	Compositions of low-molecular-weight products, %				
	HMDS	D ₄	V ₄	A ₃	A _x D _y V _z *
Initial mixture	8.8	24.2	37.4	29.6	—
4 min	11.9	30.2	51.6	0.6	5.7
2 h	16.2	41.7	3.3	—	38.8
4 h	18.4	30.4	2.5	—	48.7
8 h	26.5	3.7	1.7	—	68.1

* Cyclosiloxanes A_xD_yV_z, where $x = 0-6$, $y = 0-6$, and $z = 0-6$ at $x + y + z = 4-6$.

The mixture was heated to 95°C under stirring, and a toluene solution of TMAS (0.15 mL, 0.0001 mol with respect to (CH₃)₄NOH) was added. The mixture was stirred at 100–105°C, and samples were taken for analysis at intervals. The compositions of the reaction-mixture samples were determined via ²⁹Si NMR spectroscopy and GLC (for the low-molecular-weight fraction). To measure the refraction index and relative viscosity of the copolymer, a sample was dissolved in toluene acidified with acetic acid and the polymer was precipitated with ethanol. The resulting polysiloxane was dried and weighed; then, the refraction index and relative viscosity of the toluene solution at 25°C were measured. The intrinsic viscosity was calculated through an equation taken from [4].

²⁹Si NMR spectra of the reaction-mixture samples were recorded in a CDCl₃ solution on a Bruker AM-360 spectrometer (71.6 MHz). To decrease the relaxation time of ²⁹Si nuclei, a standard method of adding Cr(AcAc)₃ was employed. Chemical shifts were determined with a tetramethylsilane standard. For the spectral recording, a pulse experiment in the mode of spin decoupling from protons used only in acquisition interval was performed. In this case, acquisition time was 2 s, the relaxation delay was 10 s, and the experiment time varied for each sample for the obtainment of a satisfactory signal/noise ratio (from 1024 to 8096 passes). The different structural fragments (triads) in copolymers were interpreted on the basis of the data of previous studies [5, 6].

The composition of the low-molecular-weight fraction was determined on a Kristall 5000.1 gas–liquid chromatograph with a flame ionization detector and a capillary column 30 m in length and 0.32 mm in inner diameter. The initial column temperature was 100°C, the heating rate was 10 K/min, and the final column temperature and the temperatures in the evaporator and in the detector were 300°C. A 0.5-mm-thick layer of pure PDMS was the stationary phase, helium was the mobile phase, the pressure was 100 kPa, and the flow rate was 40 mL/min. The mixture composition was calculated via normalization over the peak areas.

Once the equilibrium was established, the reaction mass was heated to 150°C and stirred for 30 min up to complete decomposition of TMAS, whereupon the copolymer was separated via distillation of cyclosiloxanes at reduced pressure.

The molecular weights of the copolymers were determined via GPC with the use of a Knauer pump, Shodex Styragel columns, and a refractometric detector. The calibration was performed with PS standards. Toluene was used as an eluent, and the temperature of analysis was 20 ± 0.5°C.

RESULTS AND DISCUSSION

Copolymerization of A₃, D₄ and V₄ in the Presence of HMDS

In the course of copolymerization of A₃, D₄, and V₄ in the presence of HMDS, immediately after the addition of the initiator, a homogeneous and transparent mixture of cyclosiloxanes transformed into a heterogeneous system comprising a transparent low-viscosity phase and a milk-white high-viscosity phase.

According to the GLC data (Table 1), the 95% transparent phase is a mixture of HMDS, D₄, and V₄, a result that is confirmed by the ²⁹Si NMR spectroscopy data. The NMR spectrum displays signals of HMDS ($\delta_{\text{Si}} = 7.13$ ppm), D₄ ($\delta_{\text{Si}} = -19.21$ ppm), and V₄ ($\delta_{\text{Si}} = -32.57$ and -32.66 ppm). The high-viscosity phase is a block copolymer involving methylphenyl and methylvinylsiloxo units (A and V units). The ²⁹Si NMR spectrum (Fig. 1, spectrum I) displays predominant signals of A units in AAA triads in the region of -33.8 to -34.0 ppm and of V units in VVV triads in the region of -35.1 to -35.3 ppm.

Within 15–20 min after the onset of copolymerization, the reaction mixture becomes again homogeneous and transparent, an outcome that is related to changes in the composition of the low-molecular-weight fraction and in the copolymer structure. By this time, on the chromatogram, appear peaks of cyclosiloxanes that were absent for the initial mixture (A₄, A₅, V₅, and mixed cycles A_xV_y), the signal of V₄ decreases, and the relative fractions of HMDS and D₄ increase.

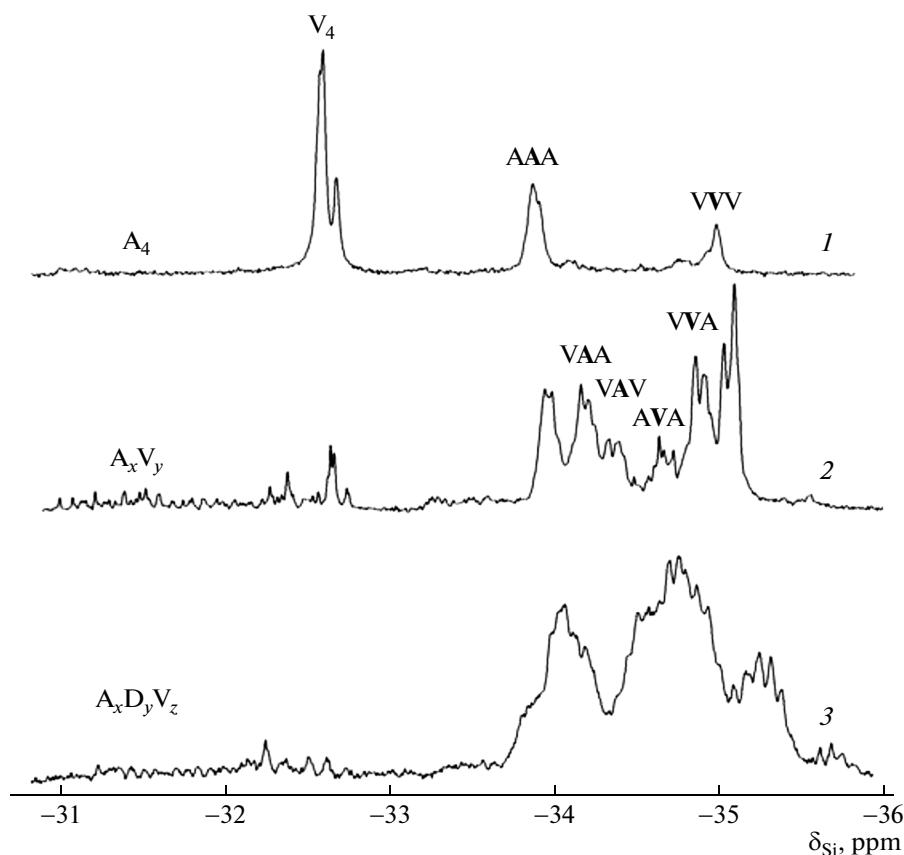


Fig. 1. Signals of A and V units in ^{29}Si NMR spectra of the products of A_3 , D_4 , and V_4 copolymerization in the presence of HMDS (1) at the beginning of the process, (2) at the end of the first stage, and (3) at the end of the second stage.

The amount of the copolymer and its molecular weight increase, and the refraction index, which is characteristic of the copolymer composition, diminishes (Fig. 2).

Because the reactivities of cyclosiloxanes change in the series $\text{A}_3 > \text{V}_4 \gg \text{D}_4$, the copolymerization proceeds in two stages. At the first stage, A_3 and V_4 enter into the reaction with almost instantaneous consumption of A_3 , whereas V_4 is consumed within 1.5–2.0 h. Throughout the first stage of the process, the copolymer is enriched in V units and, up to completion of this stage, when the conversion of V_4 exceeds 95%, the ratio of A and V units in the copolymer becomes equal to their ratio in the initial mixture of cyclosiloxanes: by this time, the random copolymer is formed (this result is confirmed by the ^{29}Si NMR spectra, displaying signals of A and V units in triads AVA, VVA, AAV, and VAV of the linear polymer) (Fig. 1, spectrum 2). The random copolymer is well compatible with mixed cyclosiloxanes. The formation of the latter compounds occurs via the equilibrium reactions of chain transfer and depolymerization.

At the second stage, D_4 gradually enters into the reaction and, in the copolymer, dimethylsiloxy units appear, that is confirmed by the signals in the ^{29}Si

NMR spectra in the region of -20.40 to -22.20 ppm, which are due to D units in triads DDD, VDD, ADD, ADA, VDA, and VDV of the linear polymer (Fig. 3). In addition, the spectra exhibit changes in the region of signals of A and V units (Fig. 1, spectrum 3). The sequence analysis of the copolymer at the triad level becomes difficult as the number of triads for each siloxane unit increases up to 6 and signals are superimposed with the formation of broad overlapping bands.

Apart from the copolymer with D units, in the reaction mixture, cyclosiloxanes involving A, V, and D units appear. The ^{29}Si NMR spectra display signals in the region of -17.00 to -20.20 ppm that are due to D units and signals in the region of -31.00 to -34.00 ppm that are due to A and V units in mixed cyclosiloxanes.

According to the data of ^{29}Si NMR and GLC, until the end of the second stage of copolymerization, the initial cyclosiloxanes, unlike HMDS, are almost completely consumed (Fig. 3). Even 8 h after the onset of the process, the intensity of the signal of HMDS ($\delta_{\text{Si}} = 7.13$ ppm) does not decrease, and its relative content in the low-molecular-weight fraction attains 26.5%. However, the molecular weight of the copolymer decreases (Fig. 2), a result that indicates the participation of HMDS in copolymerization. When the equilibrium is established, i.e., when the content of cyclic

products, their compositions, and the copolymer structure remains unchanged, the molecular weight of the copolymer according to the GPC data is 34×10^3 . This value suggests that only 5% of the initial HMDS is consumed; i.e., in this system, control over the molecular weight of copolymer by the HMDS content fails.

The low activity of the siloxane bond of HMDS toward nucleophilic agents was noted previously [7–9], and it was explained by a relatively low positive charge at the silicon atom of the trimethylsiloxy group. In the investigated system, the nucleophilicity of a propagating macroanion, which depends on the substituents at the end of the siloxane chain, must be taken into account as well: Electron-acceptor substituents (phenyl and vinyl) reduce the nucleophilicity relative to the effect of the methyl group. At the first stage of copolymerization, when only A_3 and V_4 enter into the reaction, methylphenylsiloxy or methylvinylsiloxy low-nucleophilicity units become end units of macroanions and HMDS does not participate in the reaction. At the second stage of copolymerization, when D_4 units are incorporated into the chain, the end fragment of the macroanion may be a methylsiloxane unit and the resulting active center can attack the siloxane bond of HMDS.

Copolymerization of A_3 , D_4 , and V_4 in the Presence of TMS

Copolymerization of A_3 , D_4 , and V_4 in the presence of TMS also occurs in two stages: At the first stage, A_3 and V_4 enter the reaction, and, at the second stage, D_4 enters the reaction. However, in the presence of TMS, neither turbidity nor an increase in viscosity of the reaction mass is observed: Throughout the process, the reaction mass retains homogeneity and transparency. From the aforesaid, the conclusion can be made that, at the first stage, high-molecular-weight products are not formed. In contrast, oligomers involving an average of six methylphenylsiloxy units with hydroxyl or trimethylsiloxy end groups are formed. Thus, the ^{29}Si NMR spectrum displays signals of hydroxymethylphenylsiloxy unit A^{OH} ($\delta_{\text{Si}} = -24.2$ to -24.4 ppm), A units in triads AAA ($\delta_{\text{Si}} = -33.6$ to -33.8 ppm), AAA^{OH} ($\delta_{\text{Si}} = -33.2$ to -33.4 ppm), and AAM ($\delta_{\text{Si}} = -34.05$ to -34.15 ppm) (Fig. 4). At the beginning of the first stage of polymerization, oligomethylphenylsiloxy units with hydroxyl end groups dominate, but two hours after the addition of the initiator, in ^{29}Si NMR spectra, the signals of end groups A^{OH} disappear and the signals of silicon atoms of trimethylsiloxy groups (M units) bound with methylphenylsiloxy units ($\delta_{\text{Si}} = 8.59$ ppm) and methylvinylsiloxy units ($\delta_{\text{Si}} = 8.20$ and 8.28 ppm) appear.

TMS takes an active part in copolymerization of organocyclosiloxanes owing to the active center transfer through the proton–cation exchange reaction [10].

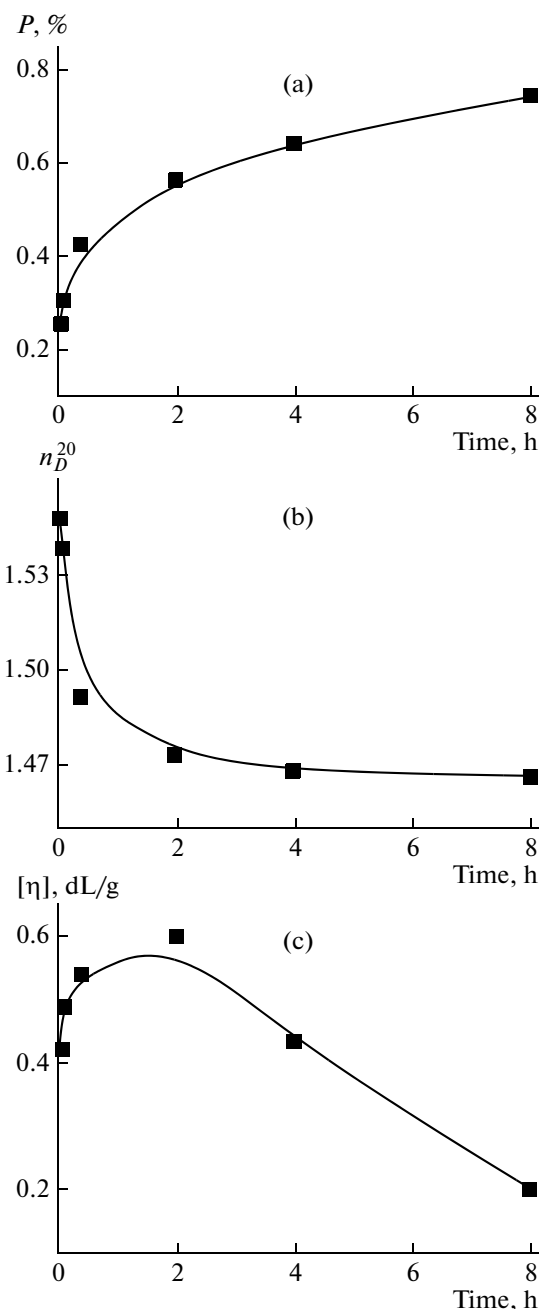
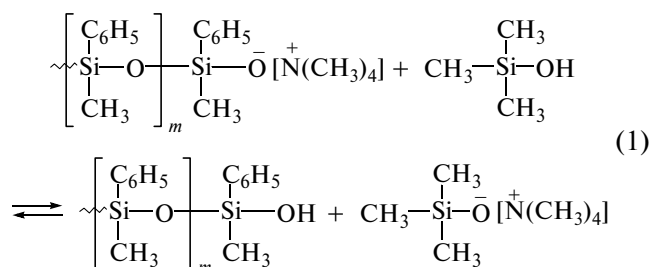


Fig. 2. (a) Copolymer yield P , (b) refractive index n_D^{20} , and (c) intrinsic viscosity $[\eta]$ in toluene at 25°C vs. polymerization time in the presence of HMDS.



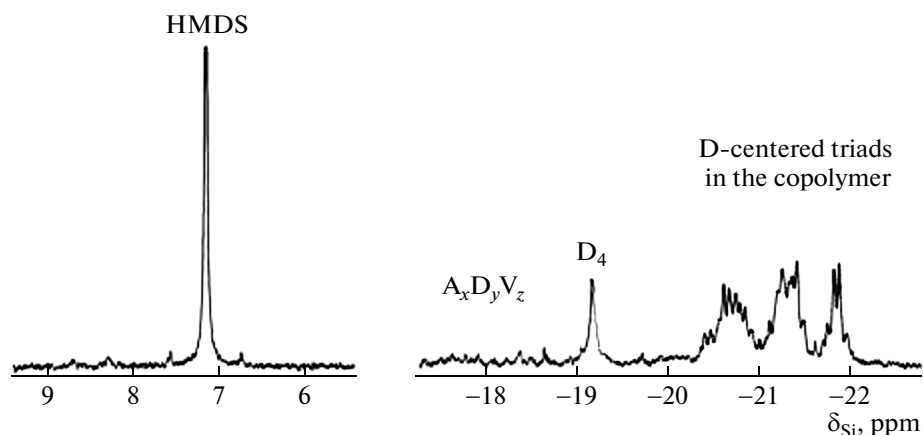


Fig. 3. Fragments of the ^{29}Si NMR spectrum of the reaction-mixture sample at the end of the second stage of A_3 , D_4 , and V_4 copolymerization in the presence of HMDS.

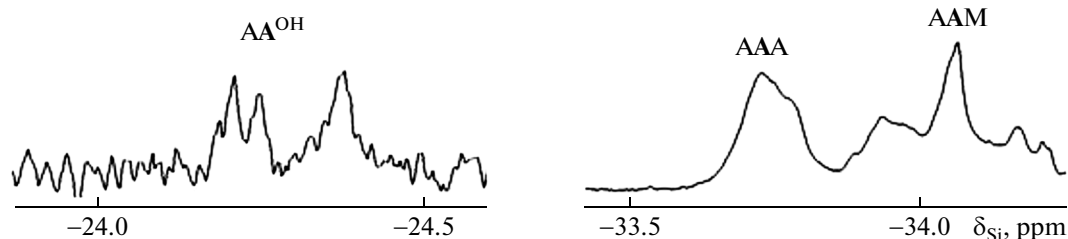
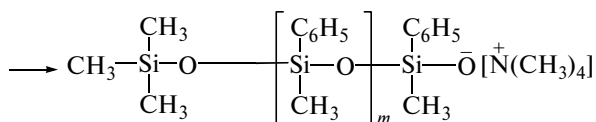
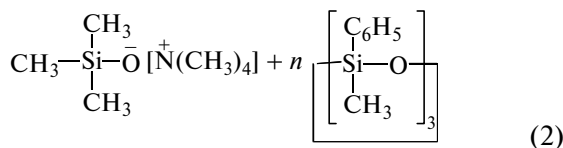


Fig. 4. Fragments of the ^{29}Si NMR spectrum of the reaction-mixture sample at the first stage of A_3 , D_4 , and V_4 copolymerization in the presence of TMS.

The resulting tetramethylammonium trimethylsil-anolate initiates polymerization of A_3 , and new a propagating molecule bears a trimethylsiloxy group at the other (inactive) end.



The proton-cation exchange (reaction (1)) proceeds rapidly; hence, the propagating macroanion manages to add one or two A_3 molecules before the chain transfer of the active center to TMS occurs. Thus, the propagating chain length is controlled. (Its length is determined by the ratio between A_3 and TMS.)

As was noted above, the number of silanol groups decreases gradually throughout this reaction owing to side reactions of silanol condensation, a result that is confirmed by water evolution at the end of the first stage of polymerization. The absence of HMDS in the reaction mixture suggests the absence of TMS homo-

condensation. As was shown previously [11], during copolymerization of hexamethylcyclotrisiloxane with TMS, the latter compound is mainly consumed in polymerization, and the condensation processes occurs only at high conversions of reagents or at a high initial TMS concentration. In our opinion, the reaction of silanol condensation makes a smaller contribution to the formation of end trimethylsiloxy groups

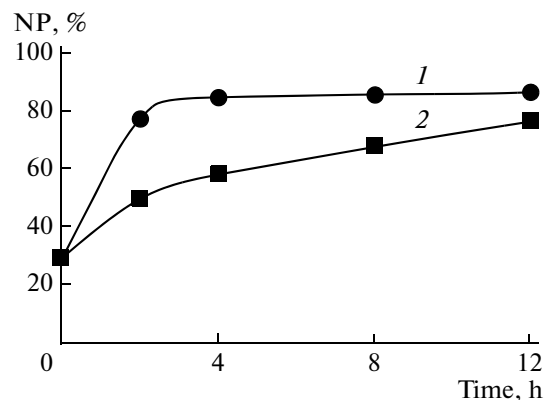


Fig. 5. Time dependence of the content of nonvolatile products (NP) of A_3 , D_4 , and V_4 copolymerization in the presence of (1) HMDS and (2) TMS.

Table 2. Properties of products* of anionic copolymerization of A₃, D₄, and V₄ in the presence of HMDS and TMS

Regulator	Refraction index n_D^{20}	Bromine number	Dynamic viscosity, mPa s (25°C)	$M_w \times 10^{-3}$ (GPC)
HMDS	1.465	76.4	1300	34.0
TMS	1.461	70.6	70	1.95
Control**	1.460	69.5	—	1.84

* After removal of cyclic compounds.

** Calculated parameters during the quantitative participation of regulators in polymerization.

because condensation results in the formation of water, and its evolution was in fact observed at later stages of the reaction when TMS was exhausted.

Thus, the main distinctive feature of copolymerization of A₃, V₄, and D₄ in the presence of TMS is the formation of a low-molecular oligomer with trimethylsiloxy end groups precisely from the beginning of the reaction. In the course of the process, the copolymer composition changes. At the first stage, the copolymer consists of A and V units and trimethylsiloxy end units in MA and MV diads. At the second stage of the reaction, dimethylsiloxy units are involved in the copolymer chain, a circumstance that is reflected by the ²⁹Si NMR spectra: signals of D units in D-centered triads of the linear copolymer (in the region of -20.40 to -22.20 ppm) and of M units bound with dimethylsiloxy units ($\delta_{Si} = 7.10$ and 7.28 ppm) appear.

Note that, during copolymerization of A₃, D₄, and V₄ in the presence of TMS, the period of time until the equilibrium is established is significantly longer than that in the presence of HMDS. Figure 5 shows that, in the copolymerization with HMDS, 2 h after the addition of the initiator, the reaction mixture contains about 22% unreacted cyclosiloxanes, whereas, in the presence of TMS, the same conversion is attained only after 12 h. As was shown previously for the example of copolymerization of D₃ and TMS, the drop in the reaction rate is related to the formation of a complex of the active center of polymerization and trimethylsilylanol as well as siloxanols formed in the course of the reaction [12].

It follows from the aforesaid that, during anionic copolymerization of A₃, D₄, and V₄, until the instant of equilibrium establishment, random copolymers with compositions determined by the ratio of the initial cyclosiloxanes are formed. Some properties of the resulting copolymers are given in Table 2. As can be seen, during copolymerization in the presence of TMS, unlike the reaction with HMDS, it has been

possible to obtain a copolymer with a molecular weight close to the calculated molecular weight.

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