

## Synthesis, rheological, and thermal properties of polydimethylsiloxanes modified with long-chain hydrocarbon substituents with polar fragments\*

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A number of polydimethylsiloxanes modified with long-chain hydrocarbon substituents with ester or benzylamide terminal groups was synthesized by hydrosilylation and polymer-analogous reactions. The copolymers were characterized by <sup>1</sup>H NMR spectroscopy, gel permeation chromatography, and differential scanning calorimetry. The influence of the type and content of modifying substituents on the low-temperature and rheological properties of the copolymers was established and indicates an increased level of intermolecular interactions in the synthesized copolymers compared to PDMS.

**Key words:** siloxane copolymers, hydrosilylation, methyl undecylenate, benzylamine, polymer-analogous reactions, rheology.

Silicones find wide use in diverse types of commercial products, such as sealants, lubricants, elastomeric materials, membranes, biomedical implantates, units of medical technique, cosmetic compositions, and others.<sup>1</sup> The predominant majority of organosilicon materials is based on polydimethylsiloxane (PDMS), which is characterized by many unique properties and a number of drawbacks preventing a broader application of this promising material. Among these drawbacks is, in particular, the low level of intermolecular interaction (IMI) resulting in low physico-mechanical characteristics of siloxane elastomeric materials.<sup>2</sup> The modification of the properties of PDMS by the introduction of various substituents at the silicon atom is one of the main directions for optimization of the properties of these materials.<sup>3–6</sup> One of the approaches leading to an increase in the IMI of the adjacent polymer chains is the introduction into the polymer of groups and fragments (particularly, polar amide, urethane, urea, *etc.*) exhibiting dipole-dipole interactions and forming hydrogen bonds. It should also be mentioned that the energy of hydrogen bonds depends on the geometry and nature of substituents in the groups involved in their formation.<sup>7</sup>

The energy of IMI of functional groups can be estimated from the heats of vaporization of the corresponding monomers. The heat of vaporization for amides is 60.6 kJ mol<sup>-1</sup>, for esters it is 18.4 kJ mol<sup>-1</sup>, whereas for R<sub>3</sub>CH it is 2.1 kJ mol<sup>-1</sup> (see Ref. 8), indicating a substantial increase in the IMI on going from simple alkyl substituents to ester and amide groups.

When using the data on the values of IMI obtained for the monomers, in polymer systems one should take into account the role of the macromolecular shape and the value of internal rotation barriers. However, it is difficult to estimate the energy of IMI in polymers because of many factors affecting this value. Therefore, the level of IMI compared to the initial analog can be estimated only by the direct study of samples of the modified polymer.

It has previously been shown<sup>9</sup> that the long-chain hydrocarbon substituents (decyl and methyl undecylenate) exert a substantial effect on a complex of physico-chemical properties of modified PDMS. When modifying units (from 5 to 15 mol.%) are introduced into the PDMS chain, the viscosity of the modified polymers and their solubility in organic solvents change substantially and the ability to form physical gels appear, which indicates an increased level of the interchain interaction in these systems.

\* Dedicated to Academician of the Russian Academy of Sciences V. I. Minkin on the occasion of his 80th birthday.

In our opinion, a logical continuation of these studies is the synthesis of PDMS containing polar groups in the modified units. The properties of the new modified PDMS will be controlled by the regulation of the number of polar substituents and the length of the hydrocarbon spacer.

The introduction of amide groups into the modifying units at the silicon atoms can be considered as one of the promising variants of the developed approach. It was shown that in polyamides<sup>10</sup> up to 99% of amide groups are involved in the hydrogen bonding, which explains high strength characteristics of polyamide fibers and materials.

This work is devoted to the synthesis and study of the rheological and thermal behavior of siloxane polymers containing long-chain hydrocarbon substituents with fragments with ester and amide groups at the silicon atoms in order to evaluate the effect of their nature and content on the level of intermolecular interaction of modified polysiloxanes.

## Experimental

Freshly distilled methyldichlorosilane, dimethyldichlorosilane, hexamethyldisiloxane, and hexamethyldisilazane were used. Sulfocation-exchange resin Purolite CT 175 was dried at 80 °C/3 mbar. Diethyl ether, sodium hydrocarbonate (reagent grade, Khimmed), and benzylamine (Aldrich, 96%) were used as received. Toluene (analytical grade, Khimmed) was dried and distilled over calcium hydride. Methyl undecylenate (Aldrich, 96%) was distilled at 71–74 °C (1 Torr) prior to use.

Gel permeation chromatography (GPC) was carried out on a chromatographic system consisting of a STAIER high-pressure pump (series 2, Akvilon, Russia), a Smartline RI 2300 refractometric detector (KNAUER, Germany), and a JETSTREAM 2 PLUS thermostat of columns (KNAUER, Germany). The temperature was maintained at 40±0.1 °C. The eluent was toluene–THF (2%), and the flow rate was 1.0 mL min<sup>-1</sup>. The columns (300×7.8 mm) were packed with the Phenogel sorbent (Phenomenex, USA) with a particle size of 5 μm and a pore size of 10<sup>4</sup> Å. The MultiKhrom 1.6 GPKh (Ampersend, Russia) was used for processing the analysis results. The columns were calibrated with polystyrene standards.

<sup>1</sup>H NMR spectra were recorded on a Bruker AV-400 spectrometer (working frequency 400.13 MHz) using CDCl<sub>3</sub> as a solvent. Chemical shifts were measured relative to tetramethylsilane.

The differential scanning calorimetry (DSC) studies were carried out on a DSC-822e instrument (Mettler-Toledo) in argon in sealed cups (sample weight ~20 mg, heating rate 10 °C min<sup>-1</sup>).

The rheological properties of synthesized polydimethylmethyl(hydro)siloxanes and modified PDMS copolymers were studied on an MCR 302 rotation rheometer (Anton Paar, Austria) using the "plane–plane" type measuring cell. The measurements in the stationary shear deformation mode were carried out at a constant shear rate of 0.1–100 s<sup>-1</sup>. The dynamic mechanical tests were carried out in the region of linear viscous elastic behavior (deformation amplitude 1%) in a frequency range of 0.1–100 Hz.

**Synthesis of PDMS modified with hydrocarbon substituents with ester groups (PDMS-E) and amide groups (PDMS-A) using the hydrosilylation reaction.** A three-necked flask (*V* = 250 mL)

equipped with a mechanical stirrer, a reflux condenser, and a dropping funnel was loaded with a 10% toluene solution of methyl undecylenate (13.9 g, 7 mmol), and a solution of Karstedt's catalyst (2 μL) in *o*-xylene (2.6 mg of Pt per 1 mL) was added. A 10% toluene solution of polydimethylmethyl(hydro)siloxane (44.0 g) containing 11.5 mol.% methyl(hydro)siloxane units (equimolar ratio of SiH and CH<sub>2</sub>=CH– groups) was added dropwise with stirring at room temperature. At the end of addition of the solution, the reaction mixture was stirred for 3–4 h at ~20 °C. The completeness of the reaction was monitored by <sup>1</sup>H NMR spectroscopy. Then hexamethyldisilazane (0.02 g) was added to remove residues of SiH and SiOH groups, the mixture was stirred for 3 h at 50 °C, and silazane residues were neutralized by trimethylchlorosilane. The obtained polymer was precipitated with methanol, and a toluene solution of the polymer was filtered through the silica gel layer to remove residues of the platinum catalyst. PDMS-E was obtained in a yield of 5.1 g (80%). <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ: 0.25 (c, (6*n* + 3) H); 0.51 (t, 2 H); 1.32 (s, 14 H); 1.65 (t, 2 H); 2.32 (t, 2 H); 3.68 (s, 3 H).

The hydrosilylation of polydimethylmethyl(hydro)siloxane copolymer with undecylenic acid benzylamide was carried out similarly. The process was conducted for 10 h at 80–85 °C. The yield of the copolymers was 75–80%. <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ: 0.25 (s, (6*n*+3) H); 0.51 (t, 2 H); 1.32 (s, 14 H); 1.69 (t, 2 H); 2.23 (t, 2 H); 4.47 (d, 2 H); 5.9–6.3 (av, 1 H); 7.25 (av, 5 H).

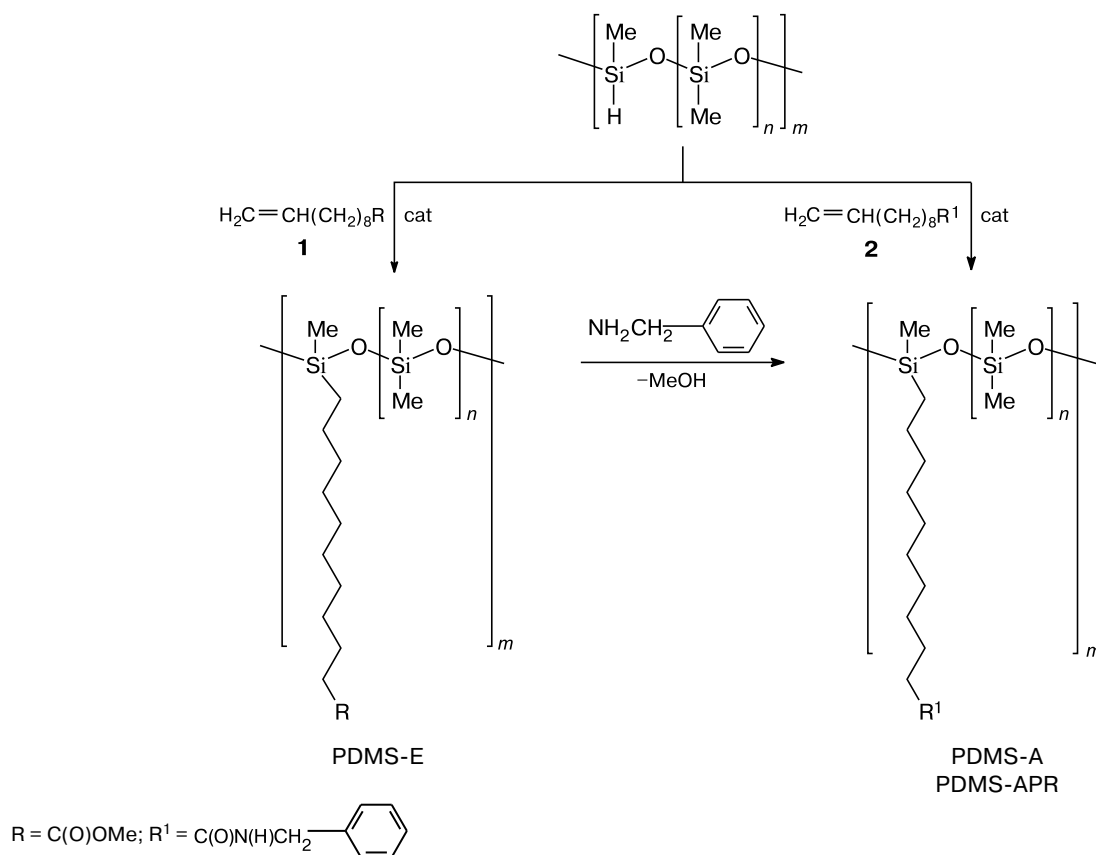
**Synthesis of PDMS modified with hydrocarbon substituents with amide groups by the polymer-analogous reaction (PDMS-APR).** A one-necked flask (*V* = 50 mL) equipped with a reflux condenser and a magnetic stirrer was loaded with PDMS-E (5.0 g) and benzylamide (12.0 g). The obtained solution was stirred for 12 h at 140 °C until the relative intensity of signals from the C(O)OCH<sub>3</sub> groups in the <sup>1</sup>H NMR spectrum stopped changing. The obtained polymer was dissolved in diethyl ether, washed with a 5% solution of hydrochloric acid to remove a benzylamine excess, and washed several times with water until the neutral pH of the aqueous layer. After the ether was removed, the polymer was dissolved in benzene and precipitated with methanol. The yield of the copolymers was 60–70%.

## Results and Discussion

**Synthesis of modified PDMS.** The polymer chain of PDMS was modified using two methods. In the first case, the long-chain hydrocarbon substituents containing polar fragments were introduced into the PDMS molecule by the hydrosilylation reaction between the Si–H groups of the polydimethylmethyl(hydro)siloxane copolymer and the corresponding agents containing an unsaturated bond (Scheme 1). The second approach consisted of polymer-analogous reactions involving the functional (ester) groups of the long-chain hydrocarbon substituents at the silicon atoms in polydimethylmethyl(methylundecylenate)siloxane copolymers obtained using the first method (see Scheme 1).

It should be mentioned that it is interesting to compare a number of physicochemical properties of modified siloxanes containing ester and amide groups in the hydrocarbon substituent at the silicon atoms and to evaluate the influence of the synthesis method on the composition and properties of the amide-containing polymers.

Scheme 1



A series of polydimethylmethyl(hydro)siloxanes with the molecular weight  $M_n$  from 10 000 to 23 000 and the content of  $\text{D}^{\text{H}}$  units from 2 to 16 mol.% was synthesized by the catalytic rearrangement of the dimethyldichlorosilane and methyldichlorosilane cohydrolysis products with hexamethyldisiloxane using the earlier described procedure.<sup>9</sup>

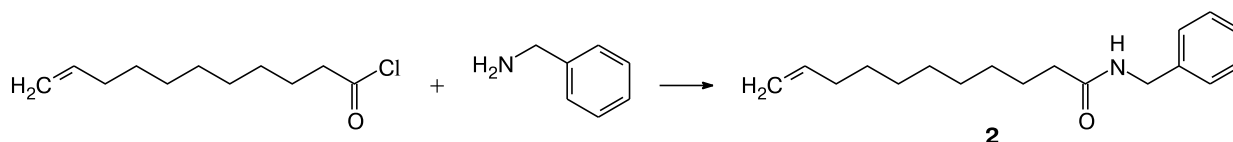
The modifying agent, undecylenic acid benzylamide (**2**), was synthesized using the known procedure<sup>11</sup> by the reaction of benzylamide with undecylenoyl chloride (Scheme 2).

The direct synthesis of the modified siloxane copolymers PDMS-E and PDMS-A was carried out using hydrosilylation by the addition of methyl undecylenate (**1**) or compound **2**, respectively, to hydride groups of polydimethylmethyl(hydro)siloxanes. The process was carried

out in a 10% solution of the components in toluene by the slow addition of a solution of polydimethylmethyl(hydro)siloxane to a solution of compound **1** or **2** in the presence of Karstedt's catalyst (see Scheme 1). The reaction course was monitored by the disappearance of signals from the Si-H and  $-\text{CH}=\text{CH}_2$  groups using  $^1\text{H}$  NMR spectroscopy.

The polymer-analogous reactions of a number of copolymers synthesized by hydrosilylation and containing methylundecylenate substituents were carried out in a benzylamine solution for 12 h at 140 °C. The reaction course was monitored by  $^1\text{H}$  NMR spectroscopy until the content of  $\text{C}(\text{O})\text{OMe}$  groups changed. It should be mentioned that the conversion of ester groups to amide groups was 86–90% and remained unchanged during further heating of the reaction mixture.

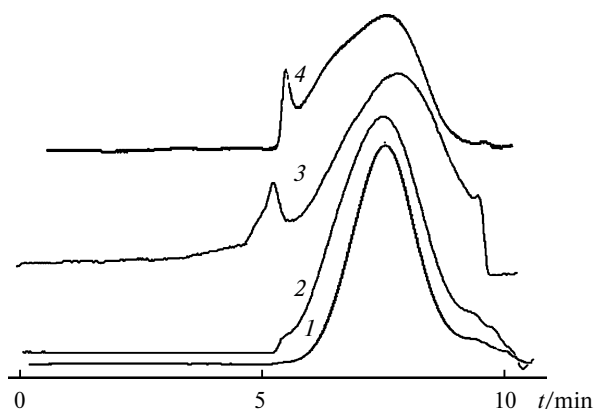
Scheme 2



Since the polymer-analogous reactions (replacement of the ester group by the amide group with the formation of modified PDMS-APR polysiloxanes) were carried out under the conditions rather drastic for polyorganosiloxanes, it was necessary to be convinced that no cleavage of the siloxane bonds of the polymer occurs. For this purpose, we performed an experiment in which the sample of narrow dispersed polydimethylsiloxane with  $M_n = 3800$  and  $M_w/M_n = 1.14$  was heated in benzylamine for 5 h at 140 °C. According to the GPC data, molecular weight of the polymer and its polydispersity remained unchanged, indicating the absence of siloxane bond cleavage reactions under the conditions of polymer-analogous reactions.

The synthesized copolymers represent viscous liquids with different degrees of opalescence, except for the samples with the maximum content of modifying amide-containing substituents, which were obtained as a rubber-like material. The composition of the obtained modified polyorganosiloxanes was determined by  $^1\text{H}$  NMR spectroscopy (Table 1).

The molecular weights of the synthesized polydimethylmethyl(hydro)siloxanes and modified PDMS were determined by GPC with respect to the linear polystyrene standards. The GPC curves of copolymers **1.2**, **2.1**, and **3.5**, which are typical of each group of the synthesized polymers, are given in Fig. 1. The molecular-weight distribution (MWD) of the modified siloxanes (PDMS-E, PDMS-A, and PDMS-APR) differs from the MWD of the initial polydimethylmethyl(hydro)siloxanes by the



**Fig. 1.** GPC curves for the initial polydimethylmethyl(hydro)siloxane (**1**) and copolymers PDMS-A (sample **3.5**, curve **2**), PDMS-APR (sample **2.1**, curve **3**), and PDMS-E (sample **1.2**, curve **4**).

character of the GPC curves in which the peak intensity increases in the area of high molecular weights and its symmetry relative to the maximum is violated.

We considered two methods for synthesis of modified PDMS with the long-chain hydrocarbon substituents containing amide fragments. In our opinion, the direct addition of the amide-containing organic modifier to the polysiloxane chain by hydrosilylation can be preferred. This modification method makes it possible to perform an almost quantitative introduction of amide-containing substituents into the PDMS chain, unlike the polymer-analogous reactions where the complete conversion of ester groups to amide groups cannot be achieved. In addition, hydrosilylation occurs under milder conditions, which makes it possible to avoid prolonged heating of polyorganosiloxane at 140 °C in a benzylamine medium, as it is assumed for polymer-analogous reactions.

**Rheological properties.** The viscoelastic characteristics of the synthesized copolymers were studied using the dynamic mechanical method. Figure 2 presents the frequency dependences of the storage modulus ( $G'$ ) and loss modulus ( $G''$ ) for samples of PDMS-E (Fig. 2, *a*) and PDMS-A (Fig. 2, *b*).

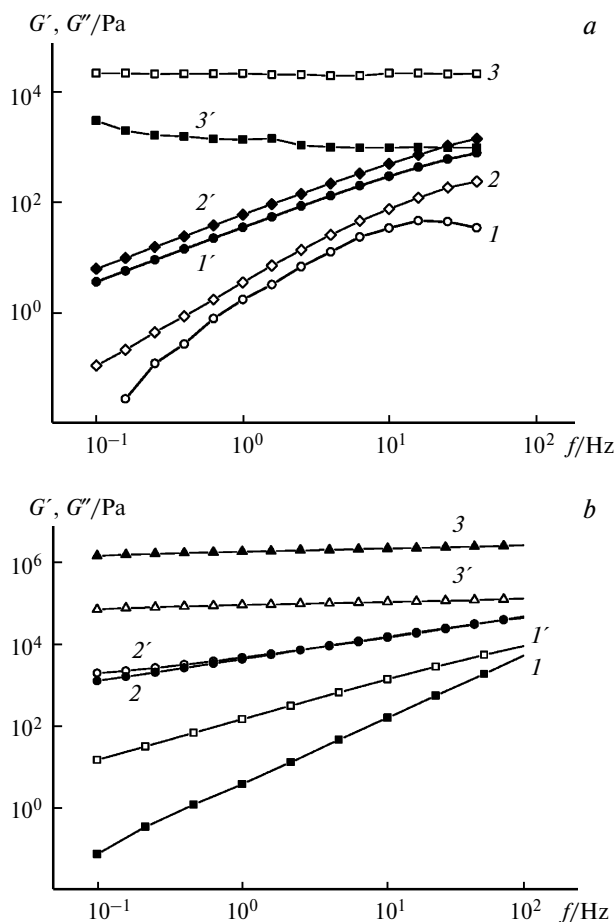
It should be mentioned that the values of  $G'$  and  $G''$  corresponding to PDMS-A are two orders of magnitude higher than the values for PDMS-E. As can be seen from the figures, at a low content of modifying units for both polymers  $G'' > G'$ , *i.e.*, the polymers are liquids from the point of view of their viscoelastic properties. As the content of the long-chain hydrocarbon substituents containing polar fragments increases, the values of  $G'$  and  $G''$  increase and crossover ( $G' = G''$ ) is observed in the curves corresponding to PDMS-A with the content of modifying units 5.3 mol.% (sample **3.5**), *i.e.*, at the frequencies higher than 1 Hz, the polymer begins to manifest the properties of elastomer. As the number of modifying units in PDMS-E increases to 16.1 (sample **1.1**) and that in

**Table 1.** Characteristics of modified polydimethylsiloxanes

Sample	D' units (mol.%)	$M_n$	$T_m$ /°C	$H_m$ /J g <sup>-1</sup>	$T_c$ /°C	$E_a$ /kJ mol <sup>-1</sup>
PDMS-E (D' = [Me(MeOC(O)(CH <sub>2</sub> ) <sub>10</sub> )SiO])						
<b>1.1</b>	16.1	16500	-63	17.1	-117	— <sup>b</sup>
<b>1.2</b>	11.3	17600	-80	11.0	-118	19.5
<b>1.3</b>	5.5	13000	-95	3.1	-120	15.8
<b>1.4</b>	2.0	20700	—	—	-123	14.0
PDMS-APR (D' = [Me(BnN(H)C(O)(CH <sub>2</sub> ) <sub>10</sub> )SiO])						
<b>2.1</b>	12.5	12500	-30	2.8	-97	39.0
<b>2.2</b>	5.3	12000	—	—	-117	30.0
<b>2.3</b>	3.9	17400	—	—	-123	24.5
<b>2.4</b>	2.0	20300	—	—	-123	24.0
PDMS-A (D' = [Me(BnN(H)C(O)(CH <sub>2</sub> ) <sub>10</sub> )SiO])						
<b>3.1</b>	14.3	16100	-10	6.5 <sup>a</sup>	-91	— <sup>b</sup>
<b>3.2</b>	11.1	10200	-12	2.5	-100	— <sup>b</sup>
<b>3.3</b>	10.0	18100	-15	9.4 <sup>a</sup>	-100	41.5
<b>3.4</b>	8.3	24700	-21	7.9	-114	38.0
<b>3.5</b>	5.3	16300	—	—	-117	—
<b>3.6</b>	4.8	14800	-29	2.8 <sup>a</sup>	-124	34.0

<sup>a</sup> Presented for the low-temperature peak in the presence of additional high-temperature endotherms.

<sup>b</sup> Elastomer.



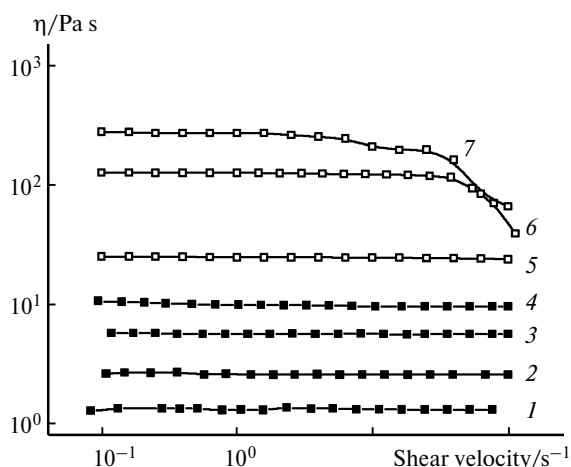
**Fig. 2.** Frequency dependences of  $G'$  (1–3) and  $G''$  (1'–3') of copolymers PDMS-E (a) and PDMS-A (b) for samples 1.4 (1, 1'), 1.2 (2, 2'), and 1.1 (3, 3').

PDMS-A increases to 11.1 mol.% (sample 3.2), both polymers are elastomers and  $G' > G''$  in the whole frequency range.

Thus, the modified PDMS with a high (>11–16 mol.%) content of modifying units are typical elastomers, and PDMS containing a minor amount of these units are viscous liquids, whose flow curves are presented in Fig. 3.

As can be seen from Fig. 4, the viscosity of the samples increases with an increase in the content of long-chain substituents with polar groups at an almost equal molecular weight of the samples. In addition, the viscosity depends weakly on the shear rate, indicating the Newtonian character of flow of the studied copolymers. It should also be mentioned that the viscosity of PDMS-A is 1–2 orders of magnitude higher than that of the unmodified polymer, and the rate of increasing viscosity with an increase in the content of modifying units in PDMS-A is higher than that for PDMS-E (see Fig. 4).

Based on the temperature dependence of the viscosity of PDMS, we calculated the activation energy of viscous flow ( $E_a$ ) using the Arrhenius equation (1). The value of  $E_a$



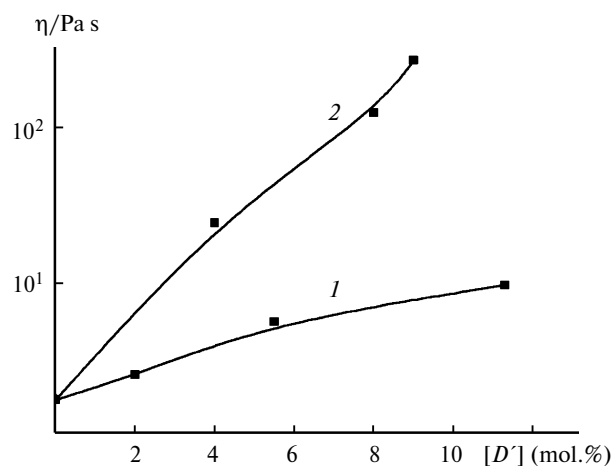
**Fig. 3.** Fluidity curves of the initial PDMS (1) and copolymers PDMS-E (sample 1.4, curve 2), PDMS-E (sample 1.3, curve 3), PDMS-E (sample 1.2, curve 4), PDMS-A (sample 3.6, curve 5), PDMS-A (sample 3.4, curve 6), and PDMS-A (sample 3.3, curve 7).

is sensitive to branches in chains of the linear polymers. The flexibility of the polymer chain, which depends on steric hindrances to the intramolecular rotation of the groups of atoms in the chain and on their interaction, exerts a determining effect on the value of  $E_a$  of the polymers. The introduction of side substituents into the polymer chain increases the sizes of the segment and induces the enhancement of  $E_a$  that characterizes the force of intermolecular interaction.

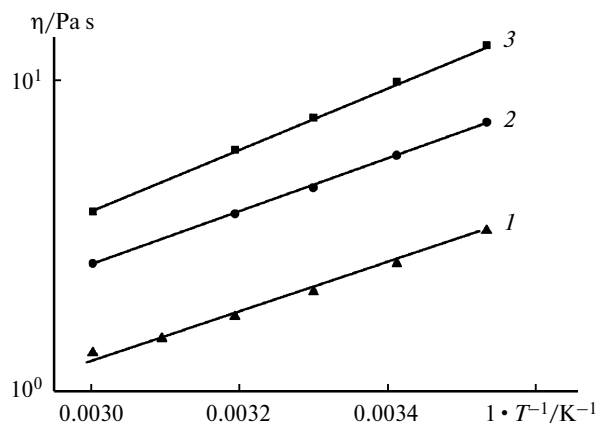
$$\eta = Ae^{E_a/RT}, \quad (1)$$

where  $\eta$  is viscosity,  $R$  is the universal gas constant, and  $T$  is temperature, K.

The temperature dependences of the viscosity of PDMS-E in the coordinates of the Arrhenius equation are



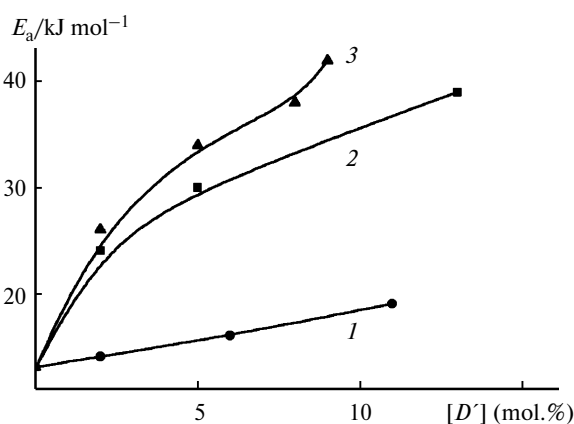
**Fig. 4.** Viscosity of PDMS-E (1) and PDMS-A (2) vs content of modifying units.



**Fig. 5.** Temperature dependences of the viscosity of PDMS-E in the Arrhenius coordinates for samples 1.4 (1), 1.3 (2), and 1.2 (3).

presented in Fig. 5 as an example. Similar dependences were also obtained for PDMS-A. As can be seen from Fig. 5, all the three dependences are straight lines, indicating constant values of  $E_a$  in this temperature range.

The influence of the content of modifying units on  $E_a$  is shown in Fig. 6. It is seen that  $E_a$  increases with an increase in the content of modifying units, and the highest values of  $E_a$  and rates of its increasing with an increase in modifying units are observed in the case of PDMS-A. The introduction into the PDMS chain of 5 mol.% of modifying units containing polar amide groups results in an increase in  $E_a$  to 41.5 kJ mol<sup>-1</sup>, which three times exceeds  $E_a$  for PDMS (14–15 kJ mol<sup>-1</sup>). It should be mentioned that the values of  $E_a$  for PDMS-APR occupy an intermediate position between the corresponding values for PDMS-E and PDMS-A, which is probably related to the copolymer structure intermediate between PDMS-E and PDMS-A because of the incompletely occurring processes of substitution of the ester group by the benzylamide group.



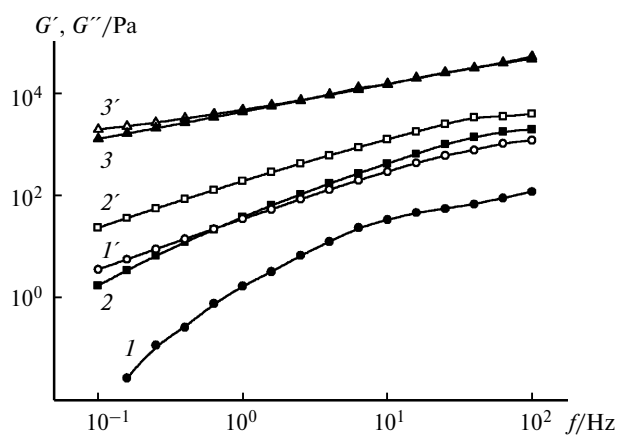
**Fig. 6.** Dependences of  $E_a$  on the content of modifying units ( $[D']$ ) in copolymers PDMS-E (1), PDMS-APR (2), and PDMS-A (3).

All polymers obtained by polymer-analogous reactions are viscous liquids even at a high (up to 12.5 mol.%) content of modifying units. The values of  $E_a$  for PDMS-APR are intermediate between the corresponding values for PDMS-E and PDMS-A. This is associated, most likely, with a specific feature of the PDMS-APR structure containing two types of polar groups at the ends of the long-chain substituents at the silicon atoms (because of the incomplete substitution of ester groups by benzylamide ones). The presence of two types of polar substituents in PDMS-APR also influences on the frequency dependences of the modified PDMS (Fig. 7) containing the same number of modifying units (about 5.5 mol.%).

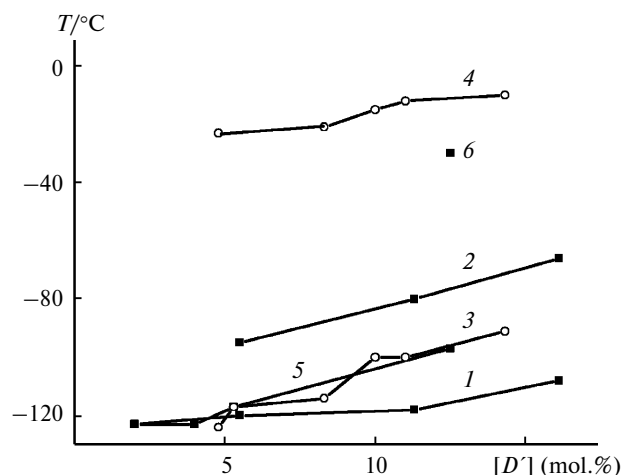
The value of  $G''$  exceeds  $G'$  for PDMS-APR and PDMS-E in the whole frequency range, whereas in PDMS-A at a certain frequency the curves are intersected and  $G'$  becomes higher than  $G''$ , which is typical of elastomers. At the same time, the values of  $G'$  and  $G''$  for PDMS-APR exceed the corresponding values for PDMS-E.

Thus, the properties of the polymers a series of PDMS-APR are intermediate between those of PDMS-A and PDMS-E, which is due to their composition including both ester and benzylamide groups at the ends of the hydrocarbon substituents at the silicon atoms.

**Analysis of temperature transitions.** The synthesized copolymers were studied by DSC. It was found that the glass transition temperature of the copolymers increases with an increase in the number of introduced modifying units, and  $T_g$  of the copolymers PDMS-A and PDMS-APR substantially exceeds this parameter for the copolymers PDMS-E (Fig. 8). Evidently, this is related to the enhancement of the intermolecular interaction on going from ester to amide terminal groups in the substituent at the silicon atoms in the modified PDMS. Note that the glass transition temperatures of the amide copolymers obtained by different methods, namely, polymer-analogous reactions or hydrosilylation, are similar (see Fig. 8, curves 3

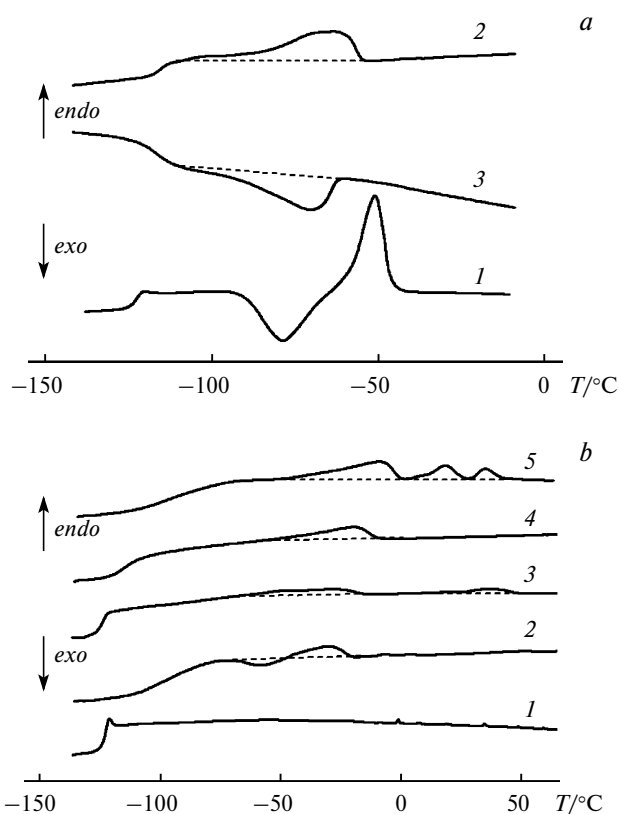


**Fig. 7.** Frequency dependences of  $G'$  (1–3) and  $G''$  (1'–3') for copolymers PDMS-E (sample 1.3, curves 1, 1'), PDMS-APR (sample 2.2, curves 2, 2'), and PDMS-A (sample 3.5, curves 3, 3').



**Fig. 8.** Glass transition (1, 3, 5) and melting (2, 4, 6) temperatures vs content of modifying units ( $[D']$ ) for copolymers PDMS-E (1, 2), PDMS-A (3, 4), and PDMS-APR (5, 6).

and 5). In addition to the jump in the heat capacity, the range of glass transition temperature of the DSC curves contained reversible endotherms (Fig. 9, *a*). As mentioned earlier,<sup>10</sup> the study of the ester-containing polydimethyl-



**Fig. 9.** DSC curves for copolymers PDMS-E (*a*) and PDMS-A and PDMS-APR (*b*) at a heating/cooling rate of  $\pm 10$  °C  $\text{min}^{-1}$ : (*a*) samples 1.4 (1) and 1.1 (2, 3); (*b*) samples 2.5 (1), 2.1 (2), 3.6 (3), 3.4 (4), and 3.1 (5).

siloxanes related this endotherm to the presence of long size methyl undecylenate fragments capable of crystallizing in the structure of the copolymers. We found similar endotherms in the DSC curves for PDMS-A, which makes it possible to attribute them to melting of the crystalline phase formed by the long aliphatic substituents with the terminal amide groups.

The observed melting temperature of the copolymers increases with an increase in the content of side substituents, and for the copolymers PDMS-A and PDMS-APR its value is higher than that for the copolymers PDMS-E (see Fig. 8, curves 4, 5, and 6). The latter is evidently a consequence of the higher melting temperature of aliphatic substituents with amide groups (according to the DSC data, the melting point of compound 2 is 65 °C) compared to the ester-containing substituents (the melting point of compound 1 is -25 °C). The value of these endotherms for PDMS-E increases with an increase in the content of the long side aliphatic substituents (see Table 1).

The thermal behavior of the ester- and amide-containing copolymers is similar by some parameters, but shows substantial differences depending on the polymer structure. For example, at the content of modifying units 2 mol.% the DSC curve of PDMS-E is the same as the corresponding curve for individual low-molecular-weight PDMS (see Fig. 9, *a*, curve 1). This curve consequently contains the jump of the heat capacity in the range of the glass transition temperature (-123 °C), the exotherm accompanying the formation of the crystalline phase of PDMS, and the melting endotherm. When the same amount of amide-containing substituents are introduced by polymer-analogous reactions, the jump in the heat capacity at -123 °C is retained in the copolymer, but the crystallization of PDMS is completely suppressed and any explicit endothermic transitions are absent from the DSC curve (see Fig. 9, *b*, curve 1). The endotherm is manifested only with an increase in the content of the side modifying units to 12.5 mol.% (see Fig. 9, *b*, curve 2). In this case, the endotherm of melting is preceded by an exotherm of cold crystallization. Thus, the formation of the crystalline phase by side amide-containing substituents is hindered in this case, whereas the crystallization of PDMS is suppressed. The direct addition of the long amide-containing substituent to PDMS *via* hydrosilylation affords polymer with glass transition temperatures close to those observed for the copolymers that were obtained by polymer-analogous reactions (see Fig. 8). However, the ability of long-chain side substituents to crystallization is manifested already at low degrees of substitution (see Fig. 9, *b*, curve 3). Note that no unambiguous dependence between the content of side substituents and the value of endotherm is observed for amide-containing polymers PDMS-A and PDMS-APR. Moreover, in some cases, additional reversible peaks appear in the DSC curves in the range of higher temperatures (see Fig. 9, *b*, curve 3), and there are multi-

ple peaks in some cases (see Fig. 9, *b*, curve 5), indicating the probable structure forming processes occurring due to specific interactions appeared upon the introduction of amide groups into the system. However, the fact that the high-temperature endotherms appear not in all polymers containing amide substituents suggests that their appearance is related to the nonuniform distribution of long-chain hydrocarbon substituents over the macromolecular chain and, correspondingly, to different contents of these substituents in the points of local crystallization. Note that the nature of this phenomenon is insufficiently studied to date and requires additional studies using methods of X-ray diffraction analysis and IR spectroscopy.

Thus, the introduction into a PDMS molecule of the long-chain hydrocarbon substituents containing polar fragments is an efficient approach to increasing the IMI, which appears as the corresponding change in the rheological characteristics and  $T_g$  of the modified polymers. The replacement of only 5 mol.% of methyl groups by amide-containing substituents results in the appearance of the properties of an elastomer in the modified PDMS.

The modification of PDMS by hydrosilylation makes it possible to synthesize copolymers with a specified content of modifying units under milder conditions compared to the polymer-analogous reaction.

It is shown that the introduction of >2 mol.% amide-containing modifying units completely suppresses the crystallization of PDMS chains, but the crystallization of the long-chain at the silicon atoms is observed.

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