

Comb-Type Methylsiloxane Copolymers with Diorganosilylene Fragments as a Lateral Group

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ABSTRACT: The catalytic dehydrocondensation reaction of α,ω -bis(trimethylsiloxy)methylhydridesiloxane and of α,ω -bis(trimethylsiloxy)methylhydridesiloxane-dimethylsiloxane with α -hydroxy- ω -trimethylsiloxydiorganosilylenes, in the presence of anhydrous caustic potassium, at 1:35 and 1:33 ratio of initial compounds has been investigated and polyorganosiloxanes with rigid polydiorganosilylenes fragment in the side chain, completely soluble in organic solvents, have been obtained. The catalytic dehydrocondensation reaction order, activation energies, and rate constants have been determined. The synthesized copolymers were

characterized by thermogravimetric, gel permeation chromatographic, differential scanning calorimetric, and wide-angle X-ray analyses. It was shown that during modification of α,ω -bis(trimethylsiloxy)methylhydridesiloxane-dimethylsiloxane with α -hydroxy- ω -trimethylsiloxydiorganosilylenes in synthesized block-copolymers, microdomain structure (phase incompatibility) was observed. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 2161–2167, 2007

Key words: methylhydridesiloxane; dehydrocondensation; polydiorganosilylenes

INTRODUCTION

It is known¹ that compounds with $\equiv\text{Si}-\text{H}$ bonds interact with water with the elimination of hydrogen in the presence of alkali catalysts. The reaction of catalytic dehydrocondensation between $\equiv\text{Si}-\text{H}$ containing compounds and hydroxyl-containing organic compounds proceeds similarly. The reaction capacity of $\equiv\text{Si}-\text{H}$ bond is determined by the nature and concentration of catalyst, temperature, reactant concentration, solvent character, etc.^{2,3}

In the reaction of catalytic dehydrocondensation of hydroxyorganosilanes with hydroorganosilanes, catalysts such as colloidal nickel, anhydrous zinc chloride, platinum hydrochloric acid, platinum on the carbon and amines^{4,5} were used and the reactions proceed according to the following scheme:



Several workers studied^{6,7} the reactions of catalytic dehydrocondensation of hydride-containing organosiloxanes with hydroxyl-containing organosilanes and organosiloxanes in the presence of powder-like caustic potassium as nucleophilic catalyst. Some workers^{8,9} have shown that under the action of nucleophilic cat-

alysts, the competing reactions of dialkylsiloxane elimination do not take place.

By catalytic dehydrocondensation of linear α,ω -dihydrideorganosiloxanes with α,ω -dihydroxydiorganosiloxane in the presence of caustic potassium, depending on the length of the siloxane fragment, both individual organosiloxanes and linear copolymers were synthesized.¹⁰ Dehydrocondensation reaction of trimethylsiloxy-group terminated ethylhydridesiloxane with hydroxyorganocyclosiloxane in the presence of caustic potassium or platinum hydrochloric acid was studied and ethylsiloxane oligomers with cyclic fragments in the side chain were obtained.¹¹ It was established that not all $\equiv\text{Si}-\text{H}$ bonds take place in dehydrocondensation reaction and various linked oligomers soluble in organic solvents were obtained. Therefore, catalytic amount of caustic potassium in dehydrocondensation reaction did not cause the opening of siloxane backbone. In the literature, there is practical information on the reaction of catalytic dehydrocondensation of hydride-containing organocyclosiloxanes with hydroxyl-containing organocyclosiloxanes.¹¹

EXPERIMENTAL

Materials and techniques

The initial α,ω -bis(trimethylsiloxy)methylhydridesiloxane, with the degree of polymerization $n = 35$, and α,ω -bis(trimethylsiloxy)methylhydridesiloxane-dimethylsiloxane were received from Fluka. α,ω -Dihydroxy-

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diorganosilylene, with various degree of polymerization, were obtained according to the literature.^{12,13} The organic solvents were cleaned by drying and distillation. The purity of the starting compounds was controlled by gas liquid chromatography "LKHM-8-MD" (Russian model), phase SKTF-100 (10%), the NAW chromosorb, carrier gas He, the 2M column.

The FTIR spectra of all samples were obtained with a Nicolet Nexus 470 machine with MCTB detector. Gel permeation chromatographic (GPC) measurements were carried out by using toluene or THF as an eluent and RI detector. Standard polystyrenes or polydimethylsiloxane were used for calibration. GPC was carried out with the use of a Waters Model 6000A chromatograph with an R 401 differential refractometer detector. The column set comprised 10^3 and 10^4 Å Ultrastayragel columns. Sample concentrations were approximately 3% by weight in toluene, and a typical injection volume for the siloxane was 5 μ L. Standardization of the GPC was accomplished by the use of styrene or PDMS standards with the known molecular weight.

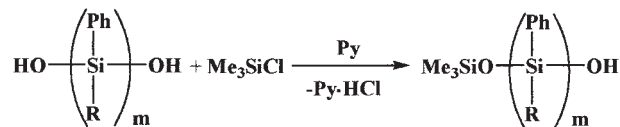
Wide angle X-ray diffractograms were obtained with a "DRON-2" (Burevestnik, Saint-Petersburg, Russia) instrument using A-Cu K α radiation. The values were measured without a filter, and the angular velocity of the motor was $\omega = 2^\circ/\text{min}$.

The differential scanning calorimetric (DSC) analyses were carried out on a Perkin-Elmer DSC-7 with a cooling accessory for the determination of thermal transitions in the polymers. Heating and cooling scanning rates were $10^\circ\text{C}/\text{min}$. The glass transition temperatures (T_g) were read from endothermic DSC traces, which were approximated to be midpoints between the extrapolated tangents to the baselines above and below the glass transition region.

The thermogravimetric investigations were carried out on a "Paulic-Pauluc-Erday" derivatograph model MOM-102. The test conditions of temperature rise rate were $5^\circ/\text{min}$, in an open area.

Heterofunctional condensation of α,ω -dihydroxyl-phenyl- α -naphthylsilylene ($n = 5$) with trimethylchlorosilane

Heterofunctional condensation reaction was carried out in a four-necked flask equipped with reflux condenser, with a two dropping funnel and mechanical stirrer. To a 10 mL dry toluene, simultaneously was added solution of 0.2897 g (0.0027 mmol) trimethylchlorosilane in 10 mL dry toluene and solution of 3.2020 g (0.0027 mmol) α,ω -dihydroxyl-phenyl- α -naphthylsilylene ($m = 5$) and 0.2136 g (0.0027 mmol) pyridine in 20 mL dry toluene at -5 to 0°C temperature. The reaction mixture was stirred for 5 h at room temperature and then heated for 2 h up to the boiling point of toluene. Then, the reaction mixture was fil-



Scheme 1 HFC of α,ω -dihydroxydiorganosilylenes with trimethylchlorosilane.

tered, washed, concentrated, and precipitated with methanol and subjected to vacuum up to constant weight. Brown-like compound I (3.2 g; 92%) was obtained. The synthesis of other monohydroxyl-derivatives was carried out analogically with the aforementioned method.

Dehydrocondensation reaction of α -hydroxyl- ω -trimethylsiloxyphenyl-naphthylsilylanes with α,ω -bis(trimethylsiloxy)methylhydridesiloxane

Catalytic dehydrocondensation reaction was carried out in a two-necked flask equipped with a catalyst inlet tube and reflux condenser connected with a gasometer. Between the gasometer and the reflux condenser, a cold trap and wash bottle were installed.

The reaction products were placed into the flask and dissolved in absolute toluene and thermostatted in an oil bath until constant temperature was achieved, and then the catalyst was introduced. After which, hydrogen having ceased to be released, the reaction products were washed until neutral area from used catalyst, dried over anhydrous Na_2SO_4 , precipitated from toluene solution by *n*-hexane, and subjected to vacuum up to constant weight.

RESULTS AND DISCUSSION

In the literature, there are no data about comb-type siloxane-silylene copolymers with the specified arrangement of linear diorganosilylene fragments as a lateral group.

For synthesis of new comb-type methylsiloxane copolymers with diorganosilylene fragments in the side chain in the first stage the HFC reaction of α,ω -dihydroxydiorganosilylenes with trimethylchlorosilane at 1:1 ratio of initial compounds, in the presence of anhydrous pyridine, in the temperature range -5 to 0°C in dilute solution of anhydrous toluene was carried out, and oligomeric α -hydroxyl- ω -trimethylsiloxydiorganosilylenes were synthesized. The reaction proceeds according to Scheme 1, in which R = α - C_{10}H_7 , $m = 5$ (I), 18 (II); R = Ph, $m = 26$ (III), 36 (IV).

After partial precipitation from toluene solution by methanol, the synthesized compounds are represented as white amorphous, solid systems well soluble in ordinary organic solvent. The composition and structure of hydroxyl containing compounds were de-

TABLE I
Some Physical–Chemical Properties of α -Hydroxyl- ω -trimethylsiloxydiorganosilylenes

No.	R	m polymerization degree	η_{sp}^a	d_1 (Å)	T_{melt} (°C)	OH (%) ^b	$\bar{M}^{b,c}$	Yield (%)
I	α -C ₁₀ H ₇	5	0.03	–	67–72	1.34 (1.32)	1266 (1287)	92
II	α -C ₁₀ H ₇	18	0.03	11.05	74–77	0.40 (0.38)	4282 (4400)	93
III	Ph	26	0.04	10.10	92–97	0.35 (0.33)	4838 (5150)	94
IV	Ph	36	0.04	10.10	93–99	0.26 (0.25)	6658 (6800)	95

^a In 1% toluene solution at 25°C.

^b Values indicate calculated values and those in parentheses indicate experimental values.

^c Molecular masses were determined by hydroxyl-group analyses.¹⁴

terminated by means of functional and elementary analysis, by finding of molecular masses, and by UV and FTIR spectral data. Some physical–chemical properties of the synthesized oligomers are presented in Table I.

In the FTIR spectra of oligomers, one can observe the absorption bands in the region 920 and 3200–3600 cm⁻¹, characteristic for associated and non associated ≡Si–OH groups accordingly and absorption bands for SiMe₃ groups at 840 cm⁻¹. In the UV spectra, one can observe absorption bands at 290 nm characteristic for ≡Si–Si≡ bonds.

Comb-type methylsiloxane copolymers with rigid polysilylene branching side groups were synthesized by catalytic dehydrocondensation reaction of hydroxyl containing polysilylene with trimethylsiloxy-terminated end group, with α,ω -bis(trimethylsiloxy)methylhydridesiloxane and α,ω -bis(trimethylsiloxy)methylhydridesiloxane-dimethylsiloxane copolymers at various ratio (1 : 35 and 1 : 33) in the presence of catalytic amount of anhydrous powder-like potassium hydroxide (0.1% total mass of initial reaction products), in anhydrous solution of toluene, at the temperature range 50, 60, and 70°C.

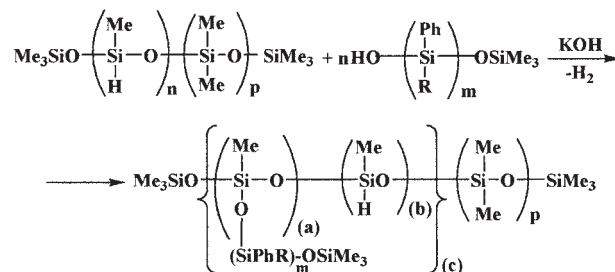
Preliminary heating of initial compounds in the temperature range 60–70°C, in the presence of 0.1% (total mass of initial reaction products) of powder-like anhydrous potassium hydroxide, showed that homo-functional condensation, elimination of methane, or cleavage of ≡Si–O–Si≡ and ≡Si–Si≡ backbone in elected condition does not take place. The reaction of catalytic dehydrocondensation proceeds according to Scheme 2. Where: [(a) + (b)](c) = $n = 35, p = 0$; (at the ratio 1:35): R = α -C₁₀H₇, $m = 5$, (V, 70°C, V², 60°C, V¹, 50°C), $m = 18$ (VI); R = Ph, $m = 26$ (VII); 36 (VIII). [(a) + (b)](c) = $n = 33, p = 25$; (at the ratio 1:33): R = α -C₁₀H₇: $m = 5$ (IX, 70°C, IX¹, 60°C, IX², 50°C); 18(X); R = Ph: $m = 26$ (XI); 36 (XII).

Copolymers, after precipitation from toluene solution by absolute *n*-hexane, represent a solid products of brown color, which are well soluble in ordinary aromatic type organic solvents with $\eta_{sp} = 0.03$ –0.33. In the FTIR spectra of synthesized copolymers, one

can observe absorption bands in the field of 2165 cm⁻¹, characteristic for unreacted ≡Si–H bonds. In the spectra are also observed absorption bands, characteristic for ≡Si–O–Si≡ bonds in the field of 1000–1100 cm⁻¹. In the UV spectra of copolymers, the absorption bands with a maximum are observed at $\lambda = 285$ nm, characteristic for ≡Si–Si≡ bonds. Some physical–chemical properties of comb-type copolymers are presented in Table II.

During catalytic dehydrocondensation of α,ω -bis(trimethylsiloxy)methylhydridesiloxane with α -hydroxyl- ω -trimethylsiloxydiorganosilylenes (at 1:35 ratio of initial compounds) in dry solution of toluene ($C = 0.01015$ mol/L), the conversion of hydrogen was determined. It was established that at the same length of trimethylsiloxy-group terminated hydroxyl-phenyl- α -naphthylsilylene with the increase of temperature from 50 to 70°C, the conversion of hydrogen rises from 85 to 95% (Fig. 1).

With an increase of the length of trimethylsiloxy-group terminated hydroxyl-phenyl- α -naphthylsilylene fragment, the reaction rate and the conversion of ≡Si–H groups in dehydrocondensation reaction decreases. The dehydrocondensation reaction actively proceeds at initial stages (the first 15 min), and then the reaction rate and the conversion of ≡Si–H groups imperceptible changes.



Scheme 2 Catalytic dehydrocondensation of hydroxyl-containing polysilylene with trimethylsiloxy terminated end group, with α,ω -bis(trimethylsiloxy)methylhydridesiloxane and α,ω -bis(trimethylsiloxy)methylhydridesiloxane-dimethylsiloxane copolymers.

TABLE II
Some Physical-Chemical Properties of Comb-type Methylsiloxane Copolymers with Diorganosilylene Fragments in Side Chain

No.	Yield (%)	React. Temp. (°C)	η_{sp}	d_1 (Å)	T_g (°C)		$M_w \times 10^{-4}$	10% mass losses (°C)	Residual mass (%)	Elementary composition ^a (%)		
					$T_{cryst.}$ (°C)	T_{melt} (°C)				C	H	Si
V	92	70	0.045	11.05	—	70–77	4.38	287	19	75.26 (75.00)	5.59 (5.12)	15.31 (14.89)
V ¹	91	60	0.043	—	—	63–69	—	—	—	77.07 (76.31)	5.18 (4.99)	14.22 (13.76)
V ^{II}	92	50	0.033	11.05	—	57–63	—	270	—	77.26 (75.44)	5.59 (5.29)	15.31 (14.80)
VI	89	70	0.33	11.05	—	76–80	—	340	12	80.61 (80.32)	5.26 (4.97)	12.97 (12.67)
VII	89	70	0.04	10.10	—	128–135	—	—	—	77.34 (76.70)	5.56 (5.30)	16.07 (15.80)
VIII	90	70	0.05	10.40	—	140–146	—	350	15	77.83 (77.47)	5.54 (5.10)	15.88 (15.45)
						–45 to						
						–122,						
						–96 to						
						to 65,						
						to 125						
IX	88	70	0.045	8.29	–86	–	–	–	–	75.80 (75.35)	5.07 (4.98)	14.44 (14.01)
IX ¹	86	60	0.041	–	–	–	–	–	–	69.86 (69.45)	6.66 (6.30)	19.10 (18.86)
IX ²	87	50	0.040	–	–	–	–	–	–	61.74 (61.42)	7.94 (7.70)	23.82 (23.29)
						–120,						
						–100 to						
						–95						
						–56 to						
						–48, 20–						
X	89	70	0.30	8.23	–95	107	–	400	23	80.41 (79.70)	5.34 (5.10)	12.79 (14.03)
						–48, 20–						
						27, 85–90						
						–48 to						
						–42, 20–						
						22, 95–						
XI	88	70	0.10	–	–120,	–	–	330	14	76.76 (76.13)	5.60 (5.24)	16.36 (15.17)
						105						
						105						
XII	86	70	0.25	10.10, 7.87	–120,	–	23.4	350	16	77.37 (77.01)	5.57 (5.06)	16.11 (15.60)

^a Values indicate calculated values and those in parentheses indicate experimental values.

Figure 2 shows a direct dependence of the reverse concentration of the reactants on the time during catalytic dehydrocondensation. It was established that at initial stages, the dehydrocondensation reaction has the second order. From this dependence dehydrocon-

denation reaction, rate constants were determined: $k_{50}^0 = 22.26$, $k_{60}^0 = 36.32$, and $k_{70}^0 = 53.61$ mol/L s.

From the dependence of logarithm of reaction rate constants on inverse temperature the activation energy of dehydrocondensation reaction was calculated, which is equal to $U_{act} = 39.1$ kJ/mol.

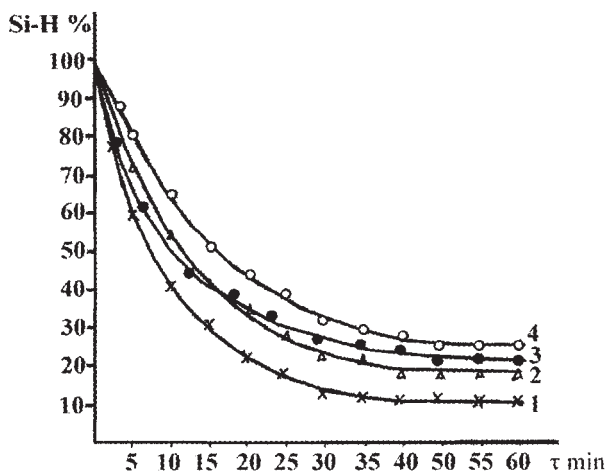


Figure 1 Dependence of changes of active $\equiv\text{Si-H}\%$ groups on the time during dehydrocondensation reaction of α,ω -bis(trimethylsiloxy)methylhydridesiloxane with trimethylsiloxy-group terminated hydroxyl-phenyl- α -naphthylsilylene ($n = 5$). Where curve 1 pertains to 70°C, curve 2 to 60°C, curve 3 to 50°C, and curve 4 pertains to ($n = 18$) at 70°C.

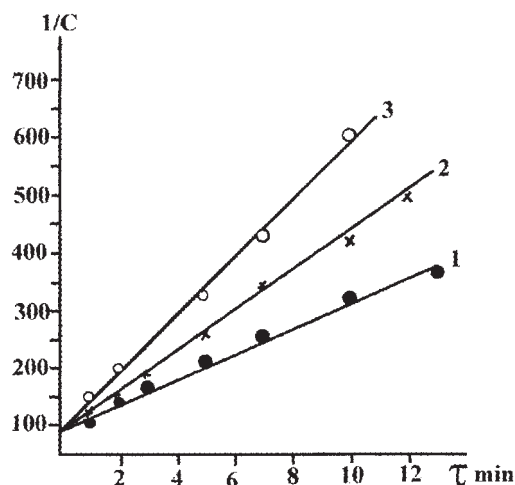


Figure 2 Dependence of inverse concentration on the time in the reaction of catalytic dehydrocondensation of methylhydridesiloxane with trimethylsiloxy-group terminated hydroxyl-phenyl- α -naphthylsilylene ($n = 5$, $C = 0.01015$ mol/L). Where curve 1 pertains to 50°C, curve 2 to 60°C, and curve 3 to 70°C.

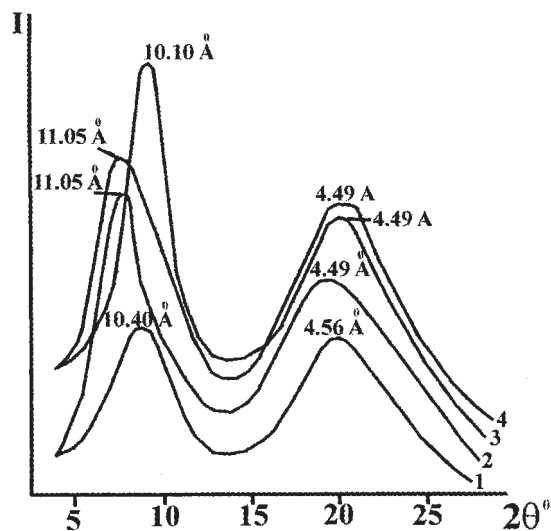


Figure 3 Wide angle X-ray patterns of comb-type siloxane-silylene copolymers, where curve 1 corresponds to copolymer VIII, curve 2 to V, 3 to VII, and 4 to VI.

X-ray diffractometry

Wide-angle X-ray analysis of synthesized copolymers was carried out. As is seen from Figure 3, comb-type copolymers (VI–VIII) are one-phase amorphous systems and are characterized only by one value of interchain distances $d_1 = 11.05$ – 9.07 Å. The given value of interchain distance should determine interchain distance between lateral branches of rigid groups, because in linear diphenylsilylene and phenyl- α -naphthylsilylene oligomers, the interchain distances are equal to 10.10–11.05 Å accordingly,¹⁵ and the interchain distance in linear oligomethylhydridesiloxane chain should not exceed 7.40 Å.¹⁶

It is necessary to note that with an increase in length of silylene fragment in lateral side group, the value of interchain distance, at identical R values, insignificantly increases 10.10 Å (copolymer VII) to 10.4 Å (copolymer VIII) and in copolymers with phenyl- α -naphthylsilylene fragments in a lateral group the interchain distance is equal to $d_1 = 11.05$ Å.

By the roentgenographic analysis for copolymers IX–XII, it is shown that on diffractogram curves, the third diffraction maximum in the region $2\theta^0 = 11.5$ – 10.75° is observed, which corresponds to values of interchain distances $d_1 = 7.70$ – 8.23 Å in flexible linear dimethylsiloxane chain. This means that here segregation processes proceeds with the formation of independent domains both for the main dimethylsiloxane chain and for lateral side groups in parallel plane (Fig. 4), which is in agreement with early stated literature data.¹⁷

Calorimetric results: DSC and TGA

For comb-type siloxane-silylene copolymers, the DSC investigations are carried out. From Figure 5, it is

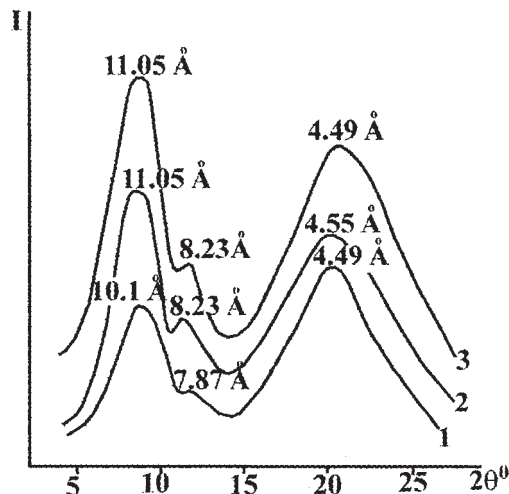


Figure 4 Wide angle X-ray patterns of comb-type siloxane-silylene copolymers, where curve 1 corresponds to copolymer XII, 2 to IX, and 3 to X.

visible that when $p = 0$, the polymers represent single-phase systems with one transition temperature in the range $T_g = 70$ – 80°C , which corresponds to glass-transition temperature of copolymers. With replacement of α -naphthyl groups by phenyl one in the rigid silylene fragment and with the increase of the length of rigid fragment, the glass-transition temperature rises. Therefore, during modification of methylhydridesiloxane oligomers with diorganosilylene fragments, the copolymers represent a continuous phase with rigid structure occupying the whole volume and discrete aggregates methylsiloxane fragments distributed in it.

Formation of the microdomain structure, two-phase systems, is observed only during modification of methylhydridesiloxane-dimethylsiloxane copolymers by rigid diorganosilylene fragments. In Figure 6, DSC curves of copolymers IX–XII are presented. Here, one can observe two glass-transition temperatures in the

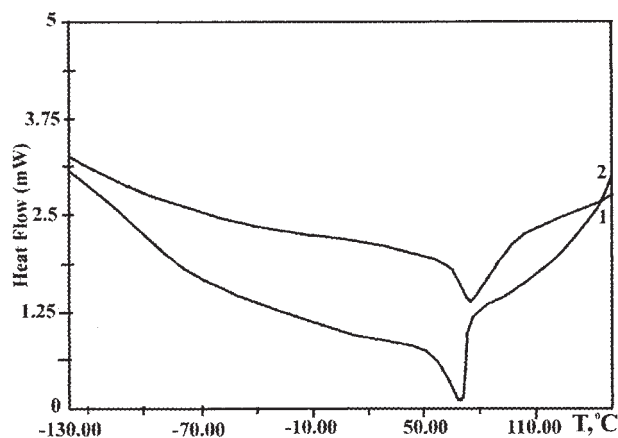


Figure 5 DSC curves of siloxane-silylene copolymers, where curve 1 corresponds copolymer V, curve 2 to VI.

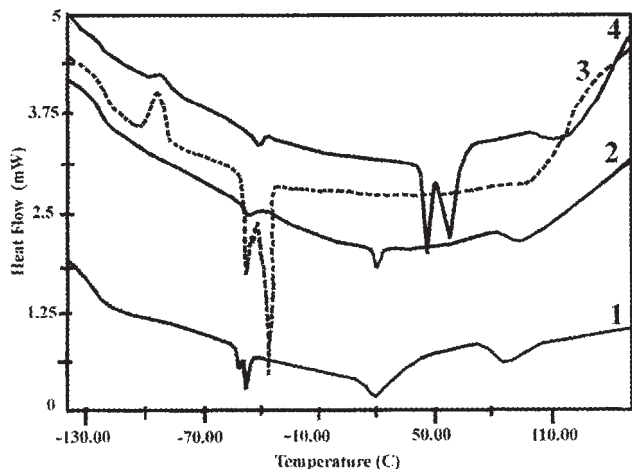


Figure 6 DSC curves of siloxane-silylene block-copolymers, where curve 1 corresponds copolymer XI, curve 2 to XII, curve 3 to X, and curve 4 to IX.

range -120 to -122°C , which is characteristic for linear PDMS chains and 20 – 65°C characteristic for rigid silylene blocks. Crystallization temperatures (T_{cryst}) in the range -86 to -100°C and melting temperatures (T_{melt}) in the range -38 to -56°C are characteristic for flexible linear PDMS blocks. One can also observe melting temperatures in the range 85 – 125°C characteristic for rigid silylene blocks.

Thus, differential-scanning calorimetric investigation confirm the conclusions made by wide-angle X-ray analysis about incompatibility of siloxane-silylene phases in comb-type BCs with rigid silylene fragments in a side chain that results in revealing properties characteristic to BCs, i.e., to two phase systems.

By thermogravimetric investigations it was established that copolymers are characterized with high thermal-oxidative stability, which may be explained with the presence of highly heat-resistant phenylo-organosilylene fragments in a side group and with their inhibiting influence on methyl groups. As it is observed from Figures 7 and 8, for copolymers, 5% mass losses are observed in the 280 – 300°C range. In these conditions, unblocked polydimethylsiloxane completely decays.¹⁸ The main destruction process proceeds in the 400 – 800°C range, and above 800°C , changes of mass loss were not observed.

On comparison of stability of copolymers and blocks-copolymers, it was established that they are characterized almost identical thermal-oxidative stability. By TGA it was shown that during introduction in the main methylsiloxane chain diorganosilylene fragments and the major destruction process begins approximately at 100°C higher than that at linear dimethylsiloxane polymers, which at 300°C completely decays. This may be explained by the presence of aromatic groups that are highly

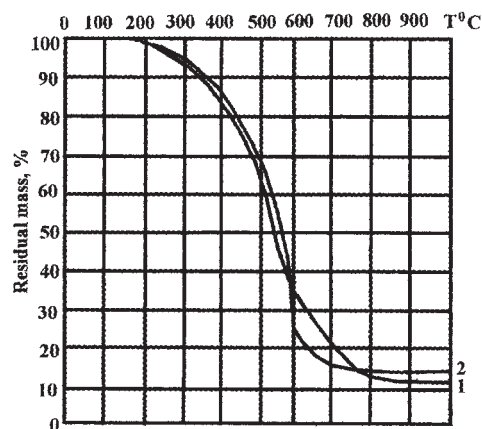


Figure 7 Thermogravimetric curves of comb-type siloxane-silylene copolymers, where curve 1 corresponds to copolymer VI and curve 2 to VIII.

resistant to oxidation and have an inhibiting effect on the oxidation of methyl groups^{18,19} and by the break of the spiral structure of the linear PDMS chain.²⁰ Moreover, the insertion of rigid diorganosilylene fragments in the side chain leads to breakdown of the destruction processes of the depolymerization mechanism, because of the impossibility of the formation of a transitive complex, which is in agreement with literature data.²¹

Thus, by us, for the first time, comb-type methylsiloxane copolymers and BCs with diorganosilylene fragments in the side chain are synthesized. It is shown that packing and segregation processes with obtaining independent domains in comb-type BCs occurs both in the main dimethylsiloxane chain and for the account of diorganosilylene fragments in side chain.

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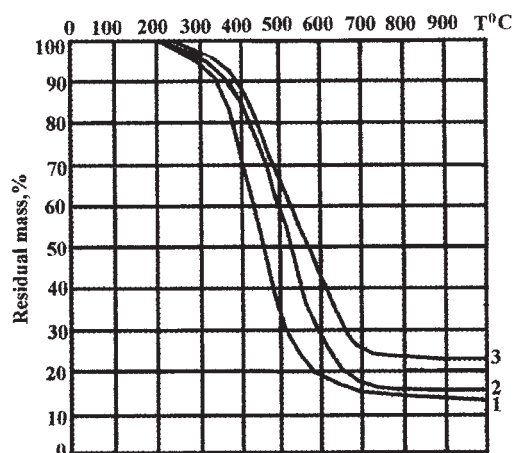


Figure 8 Thermogravimetric curves of comb-type siloxane-silylene copolymers, where curve 1 corresponds to copolymer XI, curve 2 to XII, and curve 3 to X.

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