

Arylenecyclosiloxane–Dimethylsiloxane Copolymers

O. MUKBANIANI,^{1,2} N. KOIAVA,³ M. KARCHKHADZE,¹ R. TKESHELASHVILI,¹ M. SHENGELIA,² L. KHANANASHVILI¹

¹ I. Javakhishvili Tbilisi State University, 1 I. Chavchavadze Avenue, Tbilisi 380028, Republic of Georgia

² Sukhumi State University, 12 A. Djikia Street, Tbilisi 380087, Republic of Georgia

³ Tbilisi Medical State University, 33 V. Pshavela Avenue, Tbilisi 380077, Republic of Georgia

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ABSTRACT: The heterofunctional condensation reaction of 1,4-bis(phenyldichlorosilyl)benzene with dihydroxydiphenylsilane at a 1:4 ratio of initial compounds in the presence of pyridine was investigated and tetrakis(hydroxydiphenylsiloxy)-1,4-bis(phenylsilyl)benzene was obtained. The heterofunctional condensation of the tetrakis(hydroxydiphenylsiloxy)-1,4-bis(phenylsilyl)benzene with organotrichlorosilanes at a 1:2 ratio of initial compounds in the presence of pyridine produced dichloro-containing arylenecyclosiloxanes. The dichloro-containing arylenecyclosiloxanes were obtained in one stage by successive heterofunctional condensation of 1,4-bis(dichlorophenylsilyl)benzene with dihydroxydiphenylsilane and organotrichlorosilanes in a 1:4:2 ratio in the presence of pyridine. It was established that the yields of dichloro-containing products were lower. Hydrolysis of dichloroarylenecyclosiloxanes in a neutral condition produced corresponding dihydroxy compounds. Heterofunctional polycondensation of dichloro-(dihydroxy)arylenecyclosiloxanes with α,ω -dihydroxy(bisdimethylamino)dimethylsiloxanes was used to obtain arylenecyclosiloxane-dimethylsiloxane copolymers. Thermogravimetric, thermomechanical, and roentgenographic investigations of the synthesized copolymers were carried out. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 3142–3148, 2001

Key words: arylenecyclosiloxanes; heterofunctional condensation

INTRODUCTION

It is known that by the insertion of arylene fragments in the silicon backbone causes the physical–chemical indexes and thermal–oxidative stability of copolymers to rise at the expense of increasing the inductive effect and the ability to form conjugated systems of arylene groups.^{1,2}

There are copolymers that are known to have organocyclotetra(hexa)siloxane and 1,4-bis(dimethylsilyl)benzene fragments in the chain.^{3,4} Such

copolymers were obtained by heterofunctional condensation (HFC) of 1,5-dihydroxyhexaphenylcyclotetrasiloxanes with 1,4-bis(dimethylchlorosilyl)benzene in the presence of pyridine.³ In this way copolymers with various degrees of condensation were obtained by HFC of 1,7-dihydroxy-1,7-dimethyloctaphenylcyclohexasiloxane with 1,4-bis(dimethylchlorosilyl)benzene in the presence of amines at various ratios of the initial compounds.⁴ The HFC of 1,7-dihydroxy-1,7-dimethyloctaphenylcyclohexasiloxane with 1,4-bis(dimethylsilyl)benzene in the presence of a catalytic amount of caustic potassium hydroxide produced copolymers with the same structure and a higher degree of condensation was obtained.⁵

Correspondence to: O. Mukbaniani.

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EXPERIMENTAL

The organic solvents were purified by drying and distillation. The initial 1,4-bis(phenyldichlorosilyl)benzene was synthesized by a well-known method.⁶

The purity of the initial compounds was verified with gas-liquid chromatography (JIXM-8MD). The phase SKTF-100 was 10% on a NAW chromosorb, and the carrier gas was helium.

The ¹H-NMR spectra were taken on a Perkin-Elmer R-32 instrument at an operating frequency of 90 MHz with an internal standard of hexamethyldisiloxane or tetramethylsilane. The IR spectra of all the samples were taken on an UR-20 spectrophotometer.

The thermomechanical curves were obtained on a custom-made installation. The temperature was raised at a rate of $\approx 5^\circ/\text{min}$, and the tensile strength was $\approx 0.5 \text{ kg/cm}^2$.

Thermogravimetric investigations were carried out on a Paulic-Pauluc-Erday derivatograph (model MOM-102). The temperature was raised at a rate of $\approx 5^\circ/\text{min}$.

A DPOH-2 instrument was used to produce diffractograms. The $A\text{-Cu}\alpha$ was measured without a filter, and the angular velocity of the motor was $\approx 2^\circ/\text{min}$.

HFC of 1,4-Bis(dichlorophenylsilyl)benzene with Dihydroxydiphenylsilane

The HFC reaction was carried out in a three-necked flask equipped with a reflux condenser, dropping funnel, and mechanical stirrer. A solution of 7.4 g (0.092 mol) of pyridine and 20.2 g (0.092 mol) of dihydroxydiphenylsilane in 300 mL of anhydrous ether was added to a solution of 10.0 g (0.023 mol) of 1,4-bis(dichlorophenylsilyl)benzene in 200 mL of anhydrous ether. The reaction mixture was stirred for 24 h, filtered, and washed to remove the traces of pyridine-hydrochloric acid, and dried over anhydrous Na_2SO_4 . After removal of the ether, 26.5 g of viscous white product was recrystallized from the toluene-heptane solution (40:60) and 13.7 g of white crystalline product **I** was obtained.

HFC of Terakis(hydroxydiphenylsiloxy)-1,4-bis(phenylsilyl)benzene with Methyltrichlorosilane

A solution of 3.0 g (0.02 mol) of methyltrichlorosilane in 30 mL of ether and a solution of 3.2 g (0.04 mol) of anhydrous pyridine in 30 mL of anhydrous

ether were added to a solution of 11.5 g (0.01 mol) of compound **I** in 150 mL of anhydrous ether in a temperature range of -5 to 10°C under stirring for 5 h. After that the reaction mixture was heated for 4 h. The residue was filtered off, the solvent was evaporated, and 12.2 g of viscous product was obtained. After distillation of 11.4 g of product in a vacuum, 5.8 g (51%) of pure product **II** was isolated.

The typical synthesis of compound **III** was carried out by the above-mentioned method.

HFC of 1,4-Bis(dichlorophenylsilyl)benzene with Dihydroxydiphenylsilane and Methyltrichlorosilane

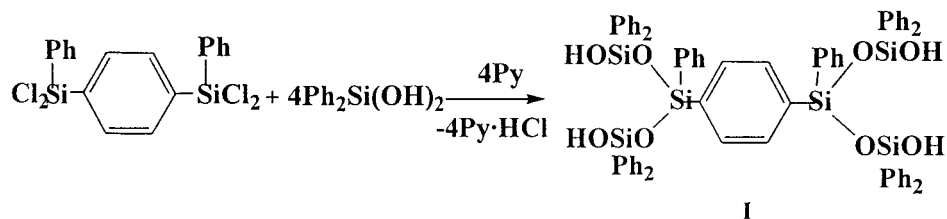
A solution of 15.0 g (0.035 mol) of 1,4-bis(dichlorophenylsilyl)benzene in 300 mL of anhydrous toluene and a solution of 10.4 g (0.07 mol) of methyltrichlorosilane in 100 mL of anhydrous toluene were gradually added to a solution of 30.28 g (0.14 mol) of dihydroxydiphenylsilane in 22.17 g (0.28 mol) of pyridine and 200 mL of dry toluene. The reaction mixture was stirred for 24 h and then heated for 4 h. The residue was filtered off, the solvent was evaporated, and 37.2 g of viscous product was obtained. After distillation of 37.2 g of the product in a vacuum we obtained 11.3 g (30.5 %) of pure product **II**. The typical synthesis of another compound **III** was carried out by the above-mentioned method.

HFC of Compound II with 1,3-Dihydroxytetramethyldisiloxane

The HFC reaction was carried out in a three-necked flask equipped with a reflux condenser, dropping funnel, and mechanical stirrer. A solution of 0.2774 g (0.0016 mol) of 1,3-dihydroxytetramethyldisiloxane and 0.2640 g (0.0032 mol) of pyridine in 2 mL of anhydrous toluene was added to a solution of 2.1709 g (0.0016 mol) of compound **II** in 3 mL of anhydrous toluene. The mixture was stirred and heated to the boiling point of toluene for 4–5 h. Then 8 mL of toluene was added. The filtered reaction mixture was washed to remove traces of pyridine hydrochloric acid, dried over anhydrous Na_2SO_4 , and reprecipitated from methanol. The product was 2.2 g (94.5%) of copolymer **VI**. The synthesis of the other copolymers was carried out by the same method.

HFC of Compound IV with α,ω -Bis(dimethylamino)dimethylsiloxane

Compound **IV** (2.41 g, 0.0019 mol) and α,ω -bis(dimethylamino)dimethylsiloxane (1.6660 g, 0.0019



Scheme 1 The first stage of the heterofunctional condensation reaction.

mol, $n \approx 8$) were placed into a reaction flask equipped with a mechanical stirrer, a hermetic seal, and a gas carrier tube (for inert gas) and stirred in the temperature range of 60–80°C until formation of a homogeneous mixture. Then the temperature was raised to 100–120°C to continue to carry out dry argon the reaction mixture was connected to the vacuum (pressure $\approx 12 \times 10^{-2}$ mmHg) up to the constant viscosity. As a result 2.9 g of copolymer **VIII** was received. The typical synthesis of other copolymers was carried out by the same method.

RESULTS AND DISCUSSION

To synthesize organosilicon copolymers with a regular alternation of arylencyclosiloxane and linear dimethylsiloxane (DMS) fragments in the chain, an investigation to obtain arylencyclosiloxane blocks with functional groups at the silicon in the cyclosiloxane fragment was carried out with the reactions in two stages. In the first stage the HFC of 1,4-bis(dichlorophenyl)silane with dihydroxydiphenylsilane at a 1:4 ratio of initial compounds in the presence of pyridine was

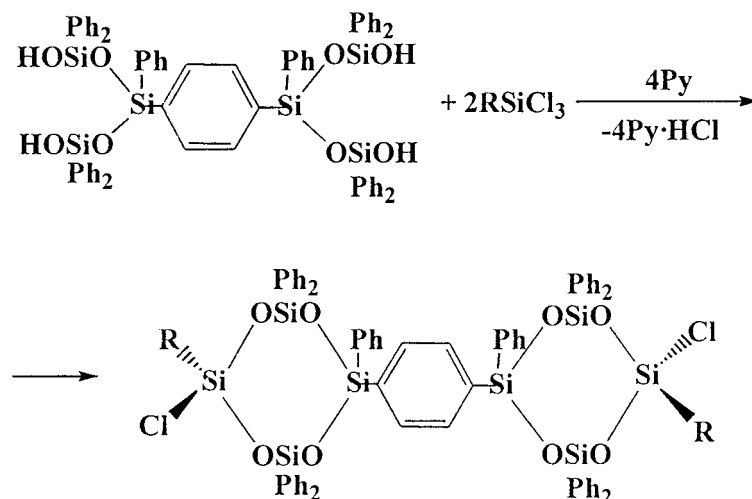
carried out in a temperature range of –5 to 10°C. After recrystallization of the reaction product from the toluene–heptane solution, a 51.6% yield of tetrakis(hydroxydiphenylsiloxy)-1,4-bis(phenylsilyl)benzene was obtained. The reaction proceeded according to Scheme 1.

In the second stage the HFC of reaction product **I** with organotrichlorosilane at a 1:2 ratio of initial compounds in the presence of pyridine was carried out in a temperature range of –5 to 10°C, and dichloroarylenecyclosiloxanes were obtained.

The reaction in this case mainly proceeded by intramolecular cyclization according to Scheme 2 where R stands for Me (**II**) or Ph (**III**).

Compounds **II** and **III** were also obtained in one stage by the HFC of 1,4-bis-(dichlorophenyl)silyl)benzene with dihydroxydiphenylsilane and organotrichlorosilanes at a 1:4:2 ratio of initial compounds in the presence of pyridine and with a temperature interval of –5 to 10°C. The yield of compounds by this method was about 32%.

The hydrolysis of dichloroarylenecyclosiloxanes (**II** and **III**) in soft conditions in the presence of sodium bicarbonate and recrystallization from toluene–heptane solution produced correspond-



Scheme 2 The second stage of the heterofunctional condensation reaction.

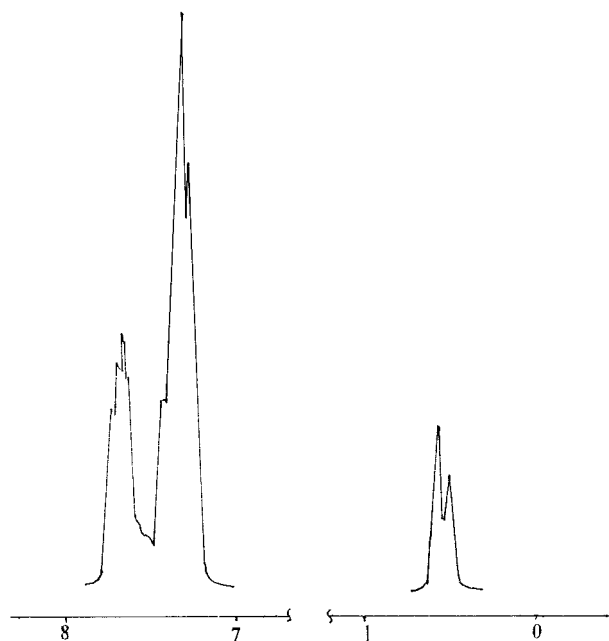
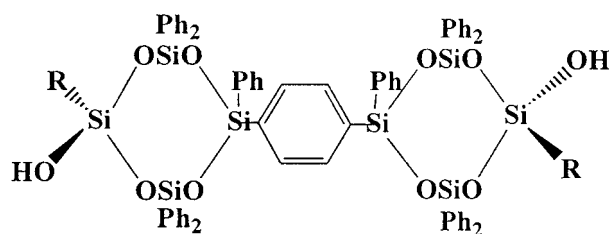


Figure 1 The $^1\text{H-NMR}$ spectra of compound I.

ing dixydroxy compounds with the following structure:



where R stands for Me (IV) or Ph (V).

The composition and structure of compounds I–V were determined by means of elementary analyses, molecular masses, and IR and $^1\text{H-NMR}$ spectral data. In the IR spectra of compounds II–V there were absorption bands at 1080 cm^{-1} that were characteristic of asymmetric valence oscillation of Si—O—Si bonds in the cyclotetrasiloxane fragment.

In the $^1\text{H-NMR}$ spectra of compound II there were observed (Fig. 1) two singlet signals with chemical shifts of 0.56 and 0.52 ppm that were characteristic for cis and trans configurations of methyl groups. The ratio of cis and trans configurations was 60 and 40% accordingly. The physical–chemical properties of the synthesized compounds are presented in Table I.

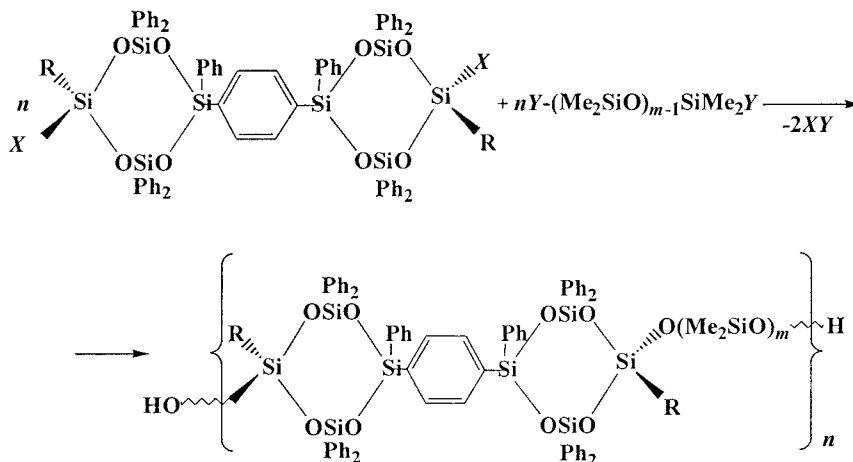
Cyclolinear copolymers with the regular arrangement of arylenecyclosiloxane fragments in the linear DMS chain were synthesized by HFC condensation of dichloroarylenecyclosiloxanes (compounds II and III) with α,ω -dihydroxydimethylsiloxanes ($n = 2,4$) in a dilute solution of anhydrous toluene in a temperature range of 20–25°C in the presence of pyridine. The reaction was completed when the reaction mixture was at the boiling point of toluene. Copolymers with high values for the length of the linear DMS chains were synthesized by HFC of compounds IV and V with α,ω -bis(dimethylamino)dimethylsiloxanes in the melt condition at 100–120°C. At the completion stage a vacuum was used until constant viscosity values were attained.

Generally the HFC reaction proceeds according to Scheme 3 in which X is Cl or OH; Y is OH or Me_2N ; R is Me and $n = 2$ (VI), 4 (VII), 8 (VIII), 18

Table I Physical–Chemical Properties of Functional Groups Containing Arylenecyclosiloxanes

Copolymer	Yield (%)	T_{boil} (°C) $1-2 \times 10^{-2}$ mmHg	T_{melt} (°C)	Elementary Composition ^a (%)				
				C	H	Si	Cl/OH	M
I	51.6	—	120–121	69.11	4.96	14.48	5.93	1146
				68.79	5.06	14.66	6.66	1020
				62.80	4.61	15.74	5.46	1299
II	51.0 (30.5)	340–345	58–60	62.08	4.96	15.81	5.17	1208
				65.77	4.49	17.24	4.98	1423
				65.13	4.21	17.36	4.75	1450
III	54.4 (32.8)	370–380	85–88	64.66	4.91	17.75	2.69	1262
				65.10	4.55	17.91	2.71	1238
				67.53	4.76	16.16	2.45	1386
IV	53.4	—	82–85	67.13	4.37	16.34	2.31	1349
				67.13	4.37	16.34	2.31	1349
				67.13	4.37	16.34	2.31	1349
V	67.2	—	95–97	67.13	4.37	16.34	2.31	1349
				67.13	4.37	16.34	2.31	1349
				67.13	4.37	16.34	2.31	1349

^a The calculated values are in the numerator, and the experimental values are in the denominator.



Scheme 3 The heterofunctional condensation reaction.

(IX), and 51 (X); or R is Ph and $n = 2$ (XI), 4 (XII), 8 (XIII), 18 (XIV), and 51 (XV).

The synthesized copolymers after reprecipitation by methanol from toluene solution were light yellow or white viscous or solid products (depending of the value n) that were soluble in organic solvents with a specific viscosity (η_{sp}) of 0.07–0.39. The molecular masses of the copolymers changed in the range of 38×10^3 to 13.5×10^4 .

Because the initial difunctional arylencyclosiloxanes (II–V) presented as a mixture of cis- and trans-isomers, the synthesized copolymers had atactic structures. By means of fractionation of copolymer VIII and elementary analysis it was proved that the reaction proceeded directionally, and the formation of copolymers had a regular arrangement of arylencyclosiloxane fragments in the chain. For copolymer VIII in the case of fraction VIII¹ (19% hole mass) the characteristic viscosity was about 0.20 dL/g, which is not typical for rigid-chain polymers⁷; the M_{SD} was 1.12×10^5 ; and the bifurcation was 6.7×10^{-10} , which practically coincided with the value of bifurcation for a linear poly(methylphenylsiloxane).⁸ The coefficient of diffusion was 11.3×10^{-7} cm²/s, the coefficient of sedimentation was 4.4, the specific volume was 0.93 cm³/g, and the increment of refraction was 0.078 cm³/g. The structure and composition of the synthesized copolymers were determined by means of elementary analysis and IR spectral data.

In the IR spectra of copolymers we observed absorption bands for asymmetric valence oscillation between 1020 and 1080 cm⁻¹, which was characteristic for Si—O—Si bonds in the linear siloxane link and the cyclo-tetrasiloxane ring, re-

spectively, which demonstrated that during HFC the ring-opening reaction of the cyclo-tetrasiloxane fragment did not take place. With the increase of the length of DMS links the absorption bands of the asymmetric valence oscillation of the methyl groups at 2900 cm⁻¹ rose compared to the valence oscillation of C—H bonds in monosubstituted phenyl groups in the range of 3030–3060 cm⁻¹. The changes of intensity were also observed at 1410 and 1435 cm⁻¹ that were characteristic for Si—Me and Si—Ph bonds, respectively. Some of the physical–chemical properties of the copolymers are presented in Table II.

Figure 2 presents the thermomechanical curves of the copolymers. As is seen from Figure 2, the replacement of the methyl groups by a phenyl one in the silsesquioxane atom of silicon in the copolymers led to a rise in the glass-transition temperature (T_g) of 10°C (see curves 2 and 7 and 4 and 5). These data conformed with an early opinion.⁹ This was explained by the considerable influence of phenyl groups whose presence anywhere in the poly(DMS) (PDMS) chain involves a rise in the T_g .¹⁰

The dependence of the T_g on the length of the linear DMS chain is presented in Figure 3. It is evident that as the length of the linear DMS chain increased the T_g of the copolymers decreased until the T_g of the linear DMS chain at about -123°C. The influence of the arylencyclosiloxane fragments on the T_g of the copolymer was obvious, including the length of the linear DMS chain ($n \approx 18$).

A thermogravimetric investigation of the synthesized copolymers was carried out. Figure 4 shows that the insertion of arylencyclosiloxane

Table II Physical-Chemical Properties of Arylenecyclosiloxane-Dimethylsiloxane Copolymers

Copolymer	Yield (%)	η_{sp} at 25°C, 1% Solution in Toluene	T_g (°C)	d_1 (Å)	5% Mass Losses (°C)	M_w ($\times 10^{-3}$)	Elementary Composition ^a (%)		
							C	H	Si
VI	93	0.08	+41	9.44	420	38	62.07	5.17	20.11
							61.69	5.03	19.76
VII	95	0.17	+30	9.41	400	—	59.22	5.15	21.82
							59.54	5.02	21.13
VIII	92	0.27	-10	—	—	87	54.90	5.88	24.40
							54.24	5.30	24.12
IX	94	0.37	-51	—	—	—	48.22	6.49	29.21
							48.03	6.13	28.79
X	96	0.39	-123	7.21	350	135	40.65	7.29	32.92
							40.22	6.86	32.68
XI	93	0.07	+54	9.87	420	—	64.90	5.01	18.46
							64.71	5.15	18.53
XII	94	0.12	+38	—	—	—	62.01	5.28	20.19
							62.25	5.37	20.61
XIII	94	0.16	-1	8.34	—	—	57.55	5.71	22.85
							57.13	5.53	22.91
XIV	95	0.23	-42	—	330	68	56.71	7.13	30.18
							56.85	7.25	30.09
XV	93	0.29	-120	7.25	—	—	42.00	7.19	32.12
							41.78	7.00	31.74

^a The calculated values are in the numerator, and the experimental values are in the denominator. The molecular masses were determined by the ebulliometric method.

fragments in the DMS chain caused the beginning mass losses observed in the temperature range of 270–280°C, but unblocked PDMS was completely destroyed in these conditions. There were 5% mass losses observed in the 400–420°C temperature region. Replacement of part of the methyl groups by a phenyl group in a silsesqui-

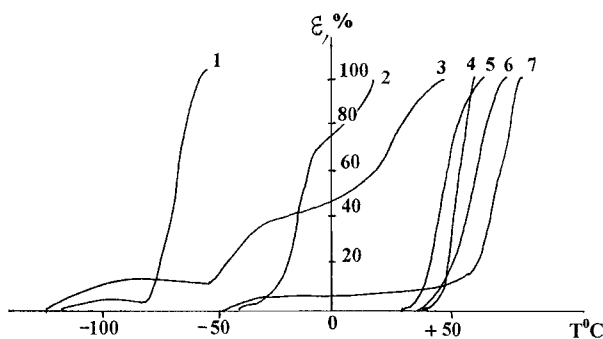


Figure 2 The thermomechanical curves of the copolymers: X (curve 1), IX (curve 2), XV (curve 3), VII (curve 4), XII (curve 5), XI (curve 6), and XIV (curve 7) (tensile strength ≈ 0.5 kg/cm²).

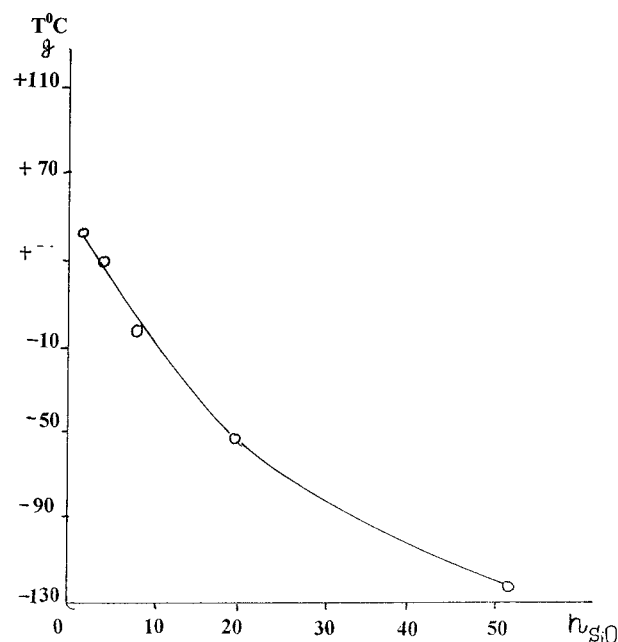


Figure 3 The dependence of the glass-transition temperature (T_g) on the length of the linear dimethylsiloxane chain.

oxane atom of silicon resulted in the rise of the decomposition starting temperature to 420°C, which is associated with the high resistance of phenyl groups to oxidation and their inhibiting effect on the oxidation of methyl groups.¹¹ The main destruction process proceeded from 450 to 700°C. After that the changes of the mass losses did not take place. The mass losses rose with the increase of the length of the linear DMS chain. With the insertion of arylene-cyclosiloxane fragments in the linear DMS chain the main destruction process proceeded at about 80–100°C higher than the destruction process of unblocked linear PDMS.

A wide-angle X-ray investigation showed (Fig. 5) that the synthesized copolymers were one-phase amorphous systems. Maximum interchain distances (d_1) were observed at small values of the length of the linear DMS chain ($d_1 \approx 9.54$ – 9.87 Å, copolymers **VI** and **XI**), and the increase of the length of the DMS chain caused the interchain distances to decrease until the interchain distances of PDMS (Fig. 5, curve 2).

The heating of copolymer **VIII** at 100–120°C in the presence of 0.1 wt % tertiary ammonium catalyst caused an anionic polymerization, and an abrupt increase of the viscosity and gel formation occurred without gas products. Changing the length of the linear DMS links between arylene-

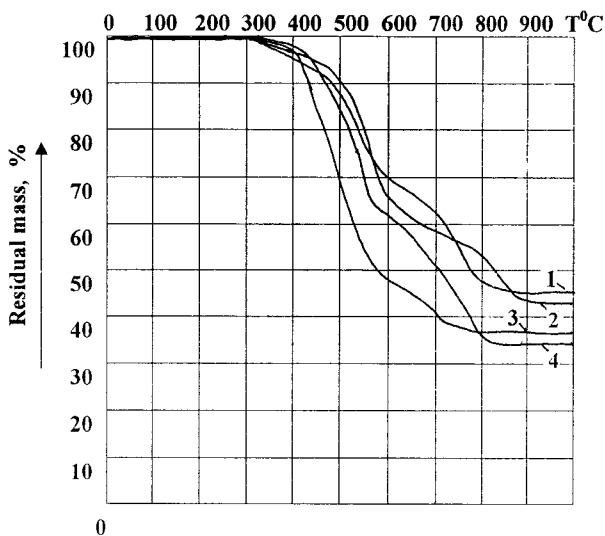


Figure 4 The thermogravimetric curves of the copolymers: **XI** (curve 1), **XII** (curve 2), **XIV** (curve 3), and **VII** (curve 4) (in an open area the temperature was raised at a rate of 5°/min).

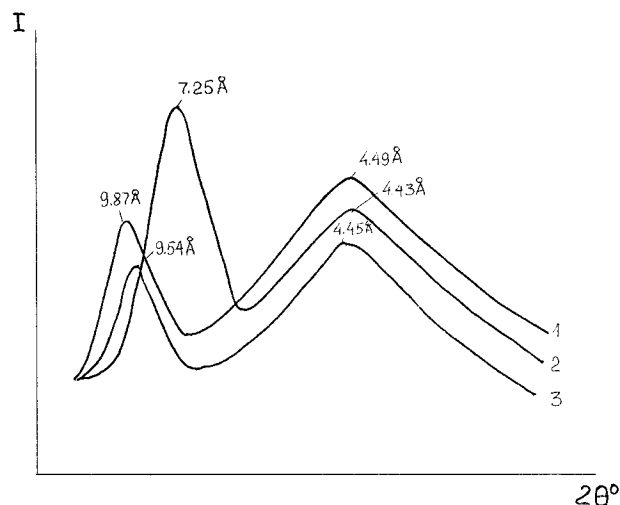


Figure 5 Diffraction patterns of the copolymers: **XI** (curve 1), **XV** (curve 2), and **VI** (curve 3).

cyclosiloxane fragments in the chain allowed the change of the average distances between the crosslink sites.

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