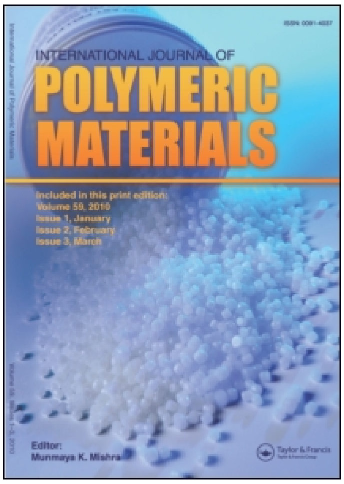

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Arylenecyclosiloxane-dimethylsiloxane copolymers

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ARYLENECYCLOSILOXANE-DIMETHYLSILOXANE COPOLYMERS

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The reaction of heterofunctional condensation (HFC) of 1,4-bis(phenyldichlorosilyl)benzene with dihydroxydiphenylsilane at initial ratio of 1:4, led to tetrakis(hydroxydiphenylsiloxy)-1,4-bis(phenylsilyl)benzene. By heterofunctional condensation of the tetrakis(hydroxydiphenylsiloxy)-1,4-bis(phenylsilyl)benzene with organotrichlorosilanes at 1:2 ratio dichloro-containing arylenecyclosiloxanes were obtained. The dichloroarylenecyclosiloxanes has been obtained by successive heterofunctional condensation of 1,4-bis(dichlorophenylsilyl)benzene with dihydroxydiphenylsilane and organotrichlorosilanes at 1:4:2 ratio. By hydrolysis of dichloroarylenecyclosiloxanes in neutral condition the corresponding dihydroxy compounds were obtained. By heterofunctional polycondensation of dichloro(dihydroxy)arylenecyclosiloxanes with α,ω-dihydroxy (bisdimethylamino)dimethylsiloxanes arylenecyclosiloxane-dimethylsiloxane copolymers were obtained. Thermogravimetric, thermomechanical and X-ray investigations of the synthesized copolymers have been carried out.

Keywords: arylenecyclosiloxane, dimethylsiloxane, copolymer

INTRODUCTION

It is known [1, 2], that by the insertion of arylene fragments in silicon backbone physical-chemical properties and thermal-oxidative stability of the copolymers rise, at the expense of increasing inductive

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Address correspondence to O. V. Mukbaniani, I. Javakhishvili Tbilisi State University, I. Chavchavadze Avenue, 1 Tbilisi 380028, Georgia. E-mail: omarimu@yahoo.com effect and the formation ability of conjugated systems of arylene groups.

From the literature, copolymers are known with organocyclotetra(hexa)siloxane and 1,4-bis(dimethylsilyl)benzene fragments in the chain [3, 4]. Such copolymers have been obtained by heterofunctional condensation of 1,5-dihydroxyhexaphenylcyclotetrasiloxanes with 1,4-bis(dimethylchlorosilyl)benzene, in the presence of pyridine [3]. By this way copolymers with various degrees of condensation have been 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 initial compounds [4]. By HFC of 1,7-dihydroxy-1,7-dimethyloctaphenylcyclohexasiloxane with 1,4-bis (dimethylsilyl)enzene in the presence of catalytic amount of caustic potassium hydroxide copolymers with the same structure and with a higher degree of condensation were obtained [5].

EXPERIMENTAL PART

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 initial compounds was verified on a gas-liquid chromatograph "XM-8M" (USSR). Phase SKTF-100(10%), on the NAW chromosorb, carrier gas helium. The ^{1}H NMR spectra were taken on a "Perkin-Elmer" R-32 instrument at an operating frequency of 90 MHz, with the internal standard HMDS or TMS. The IR spectra of all the samples were taken on a UR-20 spectrophotometer.

The thermomechanical curves were taken on a custom-made installation. The test conditions were the temperature rise rate $v \approx 5$ deg/min, $\sigma \approx 0{,}5$ Kg/cm^2.

Thermogravimetric investigations were carried out on a "Paulic-Pauluc-Erday" derivatograph, model MOM-102. The test condition was: temperature rise rate $v = 5$ deg/min.

Diffractograms were taken on a "POH-2" instrument, A-Cu$_\alpha$, were measured without a filter, the angular velocity of the motor $\omega \approx 2$ deg/min.

Heterofunctional Condensation of 1,4-Bis(Dichlorophenylsilyl)Benzene with Dihydroxydiphenylsilane

The reaction of heterofunctional condensation (HFC) was carried out in a three-necked flask equipped with a reflux condenser, dropping funnel and mechanical stirrer. To a solution of 10,0 g (0,023 mole) 1,4-bis(dichlorophenylsilyl)benzene in 200 ml anhydrous ether a solution of 7,4 g (0,092 mole) pyridine and 20,2 g (0,092 mole) dihydroxydiphenylsilane in 300 ml anhydrous ether was added. The mixture was stirred for 24 h, filtered and then washed from traces of pyridine-hydrochloric acid, and dried over anhydrous Na_2SO_4. After removal of ether, 26,5 g of viscous white product was recrystallized from tolune-heptane solution (40:60) and 13,7 g white crystalline product I were obtained.

Heterofunctional Condensation of Tetrakis(Hydroxydiphenylsiloxy)-1,4-Bis(Phenylsilyl)Benzene with Methyltrichlorosilane

To a solution of 11,5 g (0,01 mole) of compound I in 150 ml anhydrous ether a solution of 3,0 g (0,02 mole) methyltrichlorosilane in 30 ml ether and a solution of 3,2 g (0,04 mole) anhydrous pyridine in 30 ml anhydrous ether were added in the temperature range $-5 \div -10°C$ and stirred for 5 h. After that the reaction mixture was warmed to R.T. over 4 hours. The residue was filtered off and the solvent was evaporated and 12,2 g viscous product were obtained. After distillation of 11,4 g of product in vacuum, 5,8 g (51%) pure product II were isolated.

The synthesis of another compound III was carried out by the above mentioned method.

Heterofunctional Condensation of 1,4-Bis(Dichlorophenylsilyl)Benzene with Dihydroxydiphenylsilane and Methyltrichlorosilane

To a solution of 30,28 g (0,14 mole) dihydroxydiphenylsilane in 22,17 g (0,28 mole) pyridine and 200 ml dry toluene a solution of 15,0 g (0,035 mole) of 1,4-bis(dichlorophenylsilyl)-benzene in 300 ml anhydrous toluene and a solution of 10,4 g (0,07 mole) methyltrichlorosilane in 100 ml anhydrous toluene were gradually added. The reaction mixture was stirred for 24 h. After that the reaction mixture was heated at boiling temp. for 4 hours. The residue was filtered off and the solvent was evaporated and 37,2 g viscous product were obtained. After distillation of 37,2 g of product in vacuum, 11,3 g (30,5%) pure product II were isolated. The typical synthesis of another compound III was carried out by this method.

Heterofunctional Condensation of Compound II with 1,3-Dihydroxytetramethyldisiloxane

The reaction of HFC was carried out in a three-necked flask equipped with a reflux condenser, dropping funnel and mechanical stirrer. To a solution of 2,1709 g (0,0016 mole) of compound II in 3 ml anhydrous toluene, a solution of 0,2774 g (0,0016 mole) 1,3-dihydroxytetramethyldisiloxane and 0,2640 g (0,0032 mole) pyridine in 2 ml anhydrous toluene was added. The mixture was stirred and heated up to the boiling temperature of toluene for 4–5 hours. After that 8 ml toluene was added. The filtered reaction mixture was washed before neutral ambience and from traces of pyridine hydrochloric acid, dried over anhydrous Na_2SO_4, reprecipitated from methanol and 2,2 g (94,5%) copolymer VI were obtained. The typical synthesis of other copolymers were carried out by the same method.

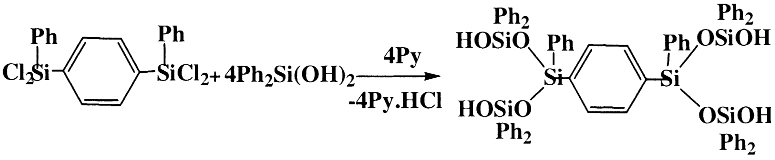
Heterofunctional Condensation of Compound IV with α,ω-Bis(Dimethylamino)Dimethylsiloxane ($n = 8$)

In a reaction flask equipped with a mechanical stirrer with a hermetic seal and a gas carrier tube (for inert gas), 2,41 g (0,0019 mole) compound IV and 1,6660 g (0,0019 mole) α,ω-bis(dimethylamino) dimethylsiloxane ($n = 8$) were placed and stirred in the temperature range $60 \div 80°C$, until formation of homogeneous mixture. Then the temperature was raised up to $100 \div 120°C$ and the reaction was continued under dry argon. The flask was connected to the vacuum ($p \approx 1\text{–}2 \times 10^{-2}$ mmHg) and the reaction continued up to constant viscosity. As a result 2,9 g copolymer VIII was obtained. The synthesis of other copolymers were carried out by the same method.

RESULTS AND DISCUSSION

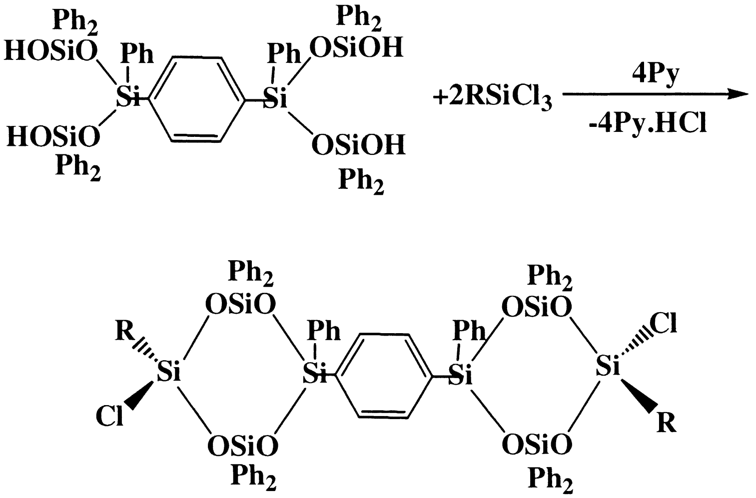
For the purpose of synthesizing organosilicon copolymers with a regular alternation of arylenecyclosiloxane and linear dimethylsiloxane fragments in the chain, studies directed at obtaining arylenecyclosiloxane blocks with functional groups at silicon in cyclosiloxane fragment were carried out in two stages. In the first stage heterofunctional condensation (HFC) was conducted of 1,4-bis (dichlorophenylsilyl)benzene with dihydroxydiphenylsilane at the ratio of initial compounds 1:4 in the presence of pyridine in the temperature interval $-5 \div -10°C$. After recrystallization, from toluene-heptane solution with a 51,6% yield of tetrakis(hydroxydiphenylsiloxy)-1,4-

bis(phenylsilyl)benzene was obtained. The reaction proceeds according to the following scheme:



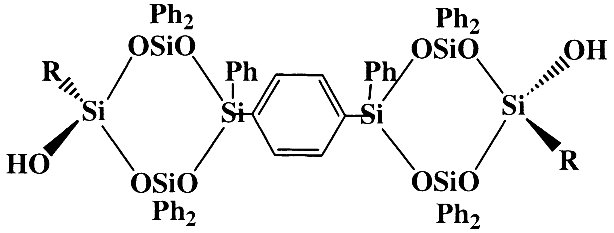
I

In the second stage HFC of the reaction product I with organotrichlorosilane at the ratio of initial compounds 1:2, in the presence of pyridine at the temperature range $-5 \div -10$°C has been carried out, and dichloroarylenecyclosiloxanes was obtained. The reaction in this case mainly proceeds by intramolecular cyclization according to the following scheme:



Where: R = Me (II), Ph(III).

Compounds II and III were also obtained in one stage by HFC of 1,4-bis-(dichlorophenylsilyl)benzene with dihydroxydiphenylsilane and organotrichlorosilanes at the ratio of initial compounds 1:4:2 in the presence of pyridine in the temperature interval $-5 \div -10°C$. The yield of compounds by this method was about $\sim 32\%$. By hydrolysis of dichloroarylenecyclosiloxanes (II,III) in soft conditions in the presence of sodium bicarbonate, and after recrystallization from toluene-heptane solution, the corresponding dihydroxy compounds has been obtained:



Where: R = Me(IV), Ph(V).

The composition and structure of compounds $I \div V$ were determined by element analyses, by molecular mass determination, by IR, and by ^1H NMR spectra data. In the IR spectra of compound II–V one can observe absorption bands at 1080 cm^{-1} characteristic for asymmetric valence oscillation of SiOSi bonds in the cyclotetrasiloxane fragment.

In the ^1H NMR spectrum of compound II one can observe (Fig. 1) two singlet signals with chemical shifts $\delta \approx 0,56$ and $\delta \approx 0,52$ ppm characteristic for cis- and trans-configuration of methyl groups. The ratio of cis- and trans-configuration are 60 and 40%, respectively. The physical-chemical properties of synthesized compounds are presented in Table 1.

Cyclolinear copolymers with the regular arrangement of arylene-cyclosiloxane fragments in linear dimethylsiloxane chain were synthesized by HFC condensation of dichloroarylenecyclosiloxanes (compounds II and III) with α,ω-dihydroxydimethylsiloxanes ($n = 2,4$), in dilute solution of anhydrous toluene, in the temperature range $20 \div 25°C$, with the heating of the reaction mixture up to the boiling point of toluene at the final stage, in the presence of pyridine. Copolymers with long linear dimethylsiloxane chain were synthesized by HFC of compounds IV and V with α,ω-bis(dimethylamino) dimethylsiloxanes in melt condition on the temperature range $100 \div 120°C$, with the use of vacuum in the final stage until constant values of viscosity.

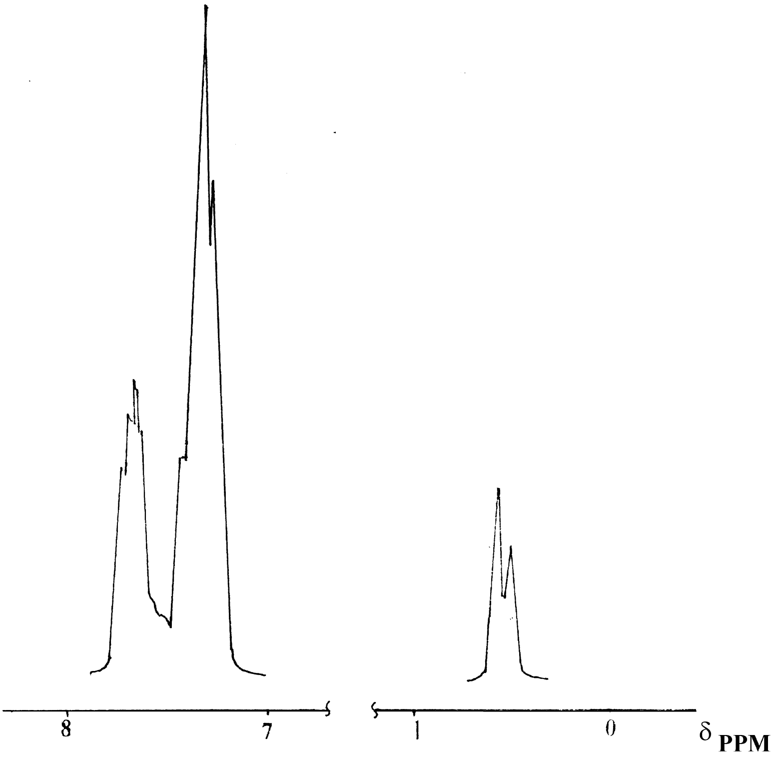
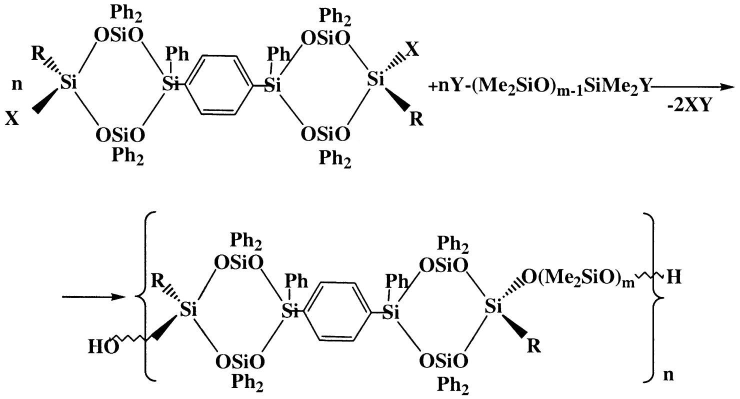


FIGURE 1 ^{1}H NMR spectra of compound 1.

TABLE 1 Physical-chemical Properties of Functional Group Containing Arylenecyclosiloxanes

No	Yield, %	T_{boil}°C, $1–2 \times 10^{-2}$, mmHg	T_{melt},°C	Elemental composition, % C	H	Si	Cl/OH	M
I	51,6	–	120–121	$\frac{69,11}{68,79}$	$\frac{4,96}{5,06}$	$\frac{14,48}{14,66}$	$\frac{5,93}{6,66}$	$\frac{1146}{1020}$
II	51,0 (30,5)	340–345	58–60	$\frac{62,80}{62,08}$	$\frac{4,61}{4,96}$	$\frac{15,74}{15,81}$	$\frac{5,46}{5,17}$	$\frac{1299}{1208}$
III	54,4 (32,8)	370–380	85–88	$\frac{65,77}{65,13}$	$\frac{4,49}{4,21}$	$\frac{17,24}{17,36}$	$\frac{4,98}{4,75}$	$\frac{1423}{1450}$
IV	53,4	–	82–85	$\frac{64,66}{65,10}$	$\frac{4,91}{4,55}$	$\frac{17,75}{17,91}$	$\frac{2,69}{2,71}$	$\frac{1262}{1238}$
V	67,2	–	95–97	$\frac{67,53}{67,13}$	$\frac{4,76}{4,37}$	$\frac{16,16}{16,34}$	$\frac{2,45}{2,31}$	$\frac{1386}{1349}$

Generally the reaction of HFC proceeds according to the following scheme:



Where: X = Cl, OH; Y = OH, Me$_2$N.

R = Me, n = 2(VI), 4(VII), 8(VIII), 18(IX), 51(X). R = Ph, n = 2(XI), 4(XII), 8(XIII), 18(XIV), 51(XV).

The synthesized copolymers after reprecipitation from toluene by methanol are light-yellow or white viscous or solid products (depending of the value of n), well soluble in organic solvents with $\eta_{sp} \approx 0{,}07 \div 0{,}39$. The molecular masses of copolymers varies in the range $M \approx 38 \times 10^3 \div 13{,}5 \times 10^4$.

Since the initial difunctional arylenecyclosiloxanes (II ÷ V) exist as a mixture of cis- and trans-isomers, the synthesized copolymers have atactic structure. By fractionation of copolymer VIII and element analysis it was proved that the reaction proceeds with the formation of copolymers having regular arrangement of arylenecyclosiloxane fragments in the chain. For copolymer VIII in the case of fraction VIII^{I} (19% of total mass) the characteristic viscosity is about $[\eta] \approx 0{,}20$ dl/g, which is not typical for rigid-chain polymers [8], $M_{SD} \approx 1{,}12 \times 10^5$, and bifurcation of this copolymers is $\Delta h/\Delta\tau \approx 6{,}7 \times 10^{-10}$, practically coinciding with the value of bifurcation for a linear polymethylphenylsiloxane [9]. Coefficient of diffusion $D \approx 11{,}3 \times 10^{-7}$ cm^2/sec, coefficient of sedimentation $S \approx 4{,}4$, specific volume $\gamma \approx 0{,}93$ cm^3/g, increment of refraction $dn/dc \approx 0{,}078$ cm^3/g. The structure and composition of the synthesized copolymers were determined by means of element analysis and by IR spectra data.

In the IR spectra of the copolymers one can observe absorption bands for asymmetric valence oscillation in the range 1020 and

1080 cm^{-1}, characteristic for ≡Si−O−Si≡ bonds in linear siloxane link and in cyclotetrasiloxane ring respectively, which indicates that during HFC the ring opening reaction of cyclotetrasiloxane fragment does not take place. With the increase in length of dimethylsiloxane links, the absorption bands of asymmetric valence oscillation of methyl groups at 2900 cm^{-1} intensify compared with valence oscillation of C−H bonds in monosubstituted phenyl groups on the range $3030 \div 3060$ cm^{-1}. The changes of intensity were also observed at 1410 cm^{-1} and 1435 cm^{-1} characteristic for ≡Si−Me and ≡Si−Ph bonds respectively. Some physical-chemical properties of the copolymers are presented in Table 2.

In Figure 2 the thermomechanical curves of the copolymers are presented. As is seen from Figure 2, replacement of the methyl groups by a phenyl one in the silsesquioxane atom of silicon in copolymers leads to a rise in glass transition temperature (T_g) by ~10°C (see curves 2,7 and 4,5), these data are in conformity with the early opinion [7]. This is explained by a considerable influence of phenyl groups whose presence anywhere in polydimethylsiloxane chain involves a rise in T_g [10].

In Figure 3 the dependence of glass transition temperature on the length of linear dimethylsiloxane chain is presented. From which it is evident that with the increase of the length of the linear dimethylsiloxane chain the T_g of copolymers decreases until the T_g of linear dimethylsiloxane chain is −123°C. The influence of arylenecyclosiloxane fragments on the T_g of copolymer is clearly evident up to the length of linear dimethylsiloxane chain of $n \approx 18$ and longer.

Thermogravimetric investigation of synthesized copolymers was carried out. As is seen from Figure 4 with the insertion of arylenecycloasiloxane fragments in dimethylsiloxane chain the beginning of mass losses is observed in the temperature range $270 \div 280$°C, while unblocked polydimethylsiloxane is completely destroyed under these conditions. 5% mass losses observed in the temperature region 400−420°C. Replacement of part of a methyl groups by phenyl one in a silsesquioxane silicon atom results in a rise of the decomposition starting temperature up to 420°C, which is associated with the high resistance of phenyl groups to oxidation as well as with their inhibiting effect on the oxidation of methyl groups [11]. The main destruction process proceeds in the temperature region $450 \div 700$°C. After that no mass loss takes place. With the increase in the length of linear dimethylsiloxane chain, the mass losses rise. With the insertion of arylenecyclosiloxane fragments in the linear dimethylsiloxane chain the main destruction process proceeds about $80 \div 100$°C higher than the destruction process of unblocked linear polydimethylsiloxane.

TABLE 2 Some Physical-chemical Properties of Arylenecyclosiloxane-dimethylsiloxane Copolymers

No copolymer	Yield, %	η_{sp}, at 25°C 1%-Solution in toulene	Tg, °C	d_1, Å	5%-mass losses, °C	$\bar{M}_w X \times 10^{-3}$	Elemental composition, %		
							C	H	Si
VI	93	0,08	+41	9,54	420	38	$\frac{62,07}{61,69}$	$\frac{5,17}{5,03}$	$\frac{20,11}{19,76}$
VII	95	0,17	+30	9,41	400	–	$\frac{59,22}{59,54}$	$\frac{5,15}{5,02}$	$\frac{21,82}{21,13}$
VIII	92	0,27	– 10	–	–	87	$\frac{54,90}{54,24}$	$\frac{5,88}{5,30}$	$\frac{24,40}{24,12}$
IX	94	0,37	– 51	–	–	–	$\frac{48,22}{48,03}$	$\frac{6,49}{6,13}$	$\frac{29,21}{28,79}$
X	96	0,39	– 123	7,21	350	135	$\frac{40,65}{40,22}$	$\frac{7,29}{6,86}$	$\frac{32,92}{32,68}$
XI	93	0,07	+54	9,87	420	–	$\frac{64,90}{64,71}$	$\frac{5,01}{5,15}$	$\frac{18,46}{18,53}$
XII	94	0,12	+38	–	–	–	$\frac{62,01}{62,25}$	$\frac{5,28}{5,37}$	$\frac{20,19}{20,61}$
XIII	94	0,16	– 1	8,34	–	–	$\frac{57,55}{57,13}$	$\frac{5,71}{5,53}$	$\frac{22,85}{22,91}$
XIV	95	0,23	– 42	–	330	68	$\frac{56,71}{56,85}$	$\frac{7,13}{7,25}$	$\frac{30,18}{30,09}$
XV	93	0,29	– 120	7,25	–	–	$\frac{42,00}{41,78}$	$\frac{7,19}{7,00}$	$\frac{32,12}{31,74}$

*In numerator calculated values and in denominator experimental values.

*Molecular masses were determined by ebulliometric method.

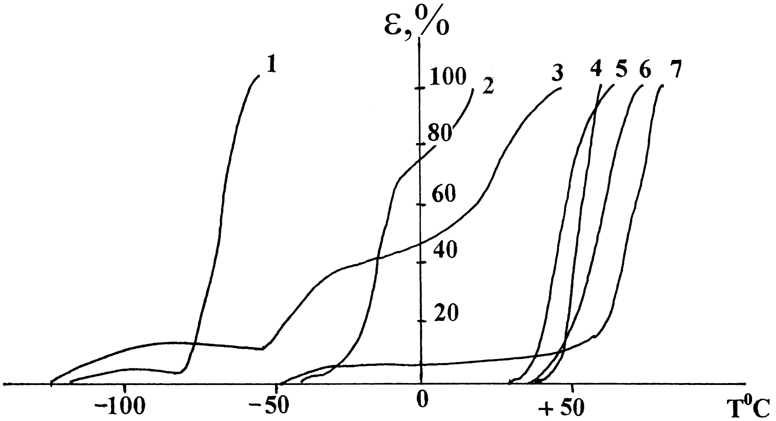


FIGURE 2 Thermomechanical curves of copolymers, where curve 1 corresponds to copolymer X, curve 2 corresponds to copolymer IX, curve 3–XV, curve 4–VII, curve 5–XII, curve 6–XI and curve 7–XIV ($\sigma \approx 0{,}5$ Kg/cm^2).

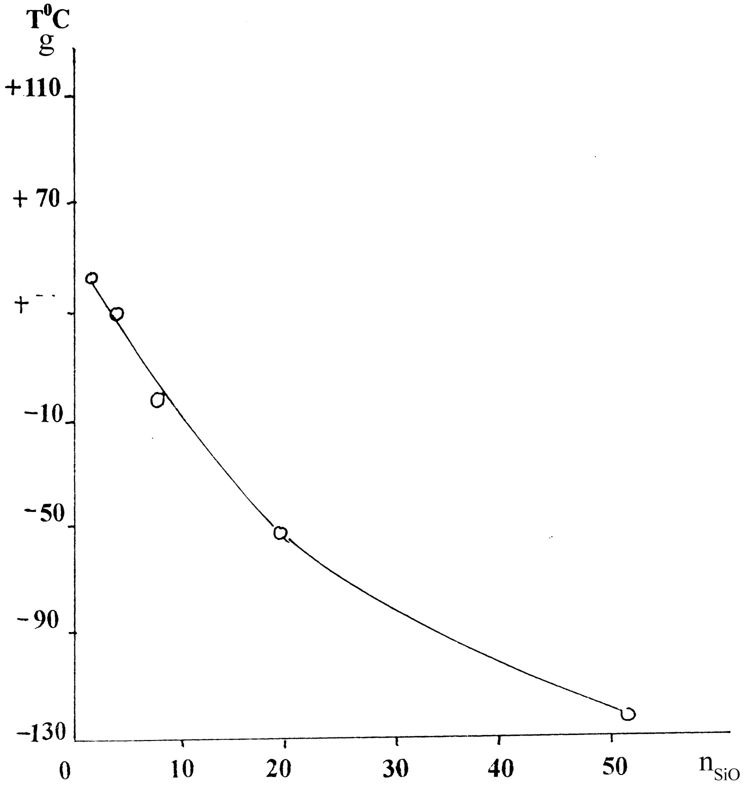


FIGURE 3 Dependence of glass transition temperature on the length of linear dimethylsiloxane chain.

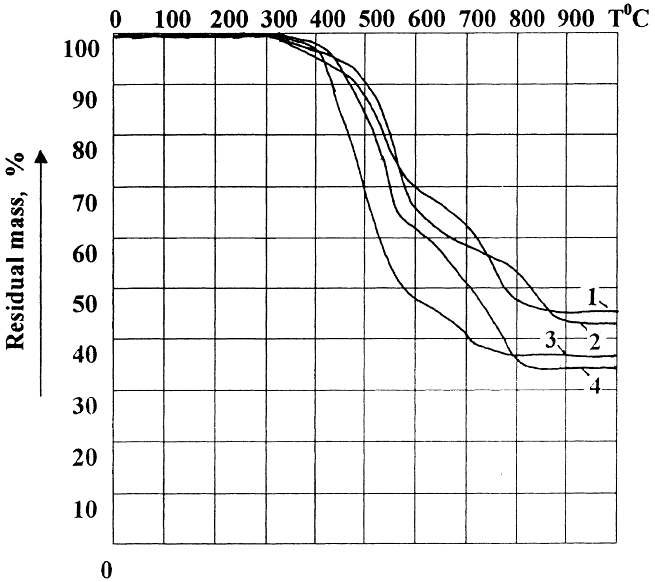


FIGURE 4 Thermogravimetric curves of copolymers, where curve 1 corresponds to copolymer XI, 2–XII, 3–XV, 4–VII (in open area, temperature rise rate v ≈ 5 deg/min).

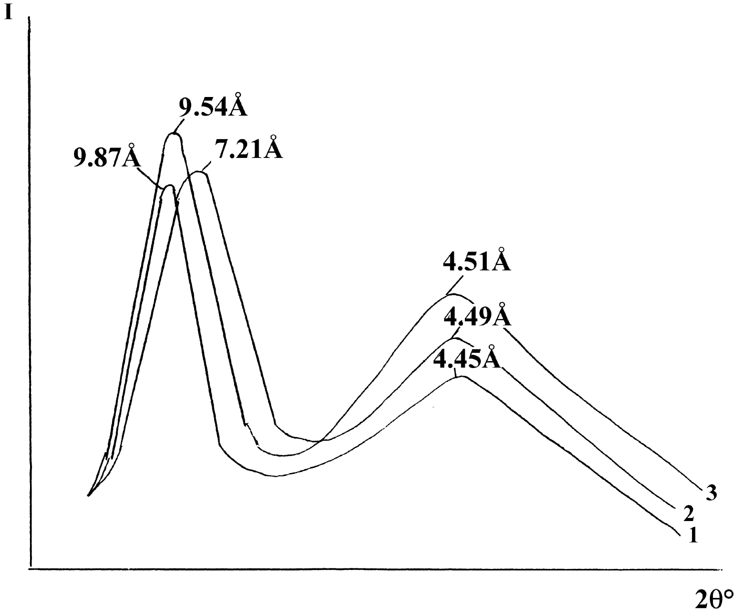


FIGURE 5 Diffractograms of copolymers, where curve 1 corresponds to copolymer XI and curve 2–XIV.

Wide angle X-ray investigation show (Figure 5) that the synthesized copolymers are one phase amorphous systems. The maximum values of interchain distances d_1 observed at a small values of a length of linear dimethylsiloxane chain ($d_1 \approx 9{,}54-9{,}87$ Å, copolymer VI and XI), with the increase of the length of dimethylsiloxane chain the interchain distances decrease until the interchain distance of polydimethylsiloxane, Figure 5 curves 3,4.

Heating of copolymer VIII at 100–120°C in the presence of 0,1 wt% tertiaryammonium catalyst, causes an anionic polymerization to take place with an abrupt increase of viscosity and gel formation, without the production of gas by-products. By changing the length of linear dimethylsiloxane links between arylenecyclosiloxane fragments in the chain, one may change the average distance between the crosslink sites.

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