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Cycloliner Copolymers with Biscyclic Fragments in the Side Chain

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The reaction of heterofunctional condensation of hydroxymethyl(phenyl)cyclosiloxanes with tetrachlorosilane in the ratio 2:1 of initial products has been studied in the presence of pyridine and bis(heptamethylcyclotetrasiloxyl)dichlorosilane and bis(pentaphenylcyclotrisiloxyl)dichlorosilane were obtained. The reaction of heterofunctional condensation of bis(organocyclosiloxyl)dichlorosilanes with α,ω -dihydroxydimethylsiloxanes in the presence of pyridine was investigated. It was shown that at small lengths of the linear dimethylsiloxane links, the reaction of heterofunctional condensation runs both intermolecularly with formation of polymers and intramolecularly with formation of tricycloorganosiloxanes. It was established, that the insertion of bis organocyclosiloxyl fragments in the side chain hinders the chain transfer reactions that proceed with release of the D-type cycles during thermal depolymerization. Thermogravimetric, thermo-mechanical and X-ray studies of synthesized copolymers were carried out.

Keywords: Organosiloxane copolymers; heterofunctional condensation; thermal-oxidative stability

INTRODUCTION

Polydimethylsiloxanes (PDMS) are widely used for preparation of heat resistant rubbers. On the basis of these elastomers heatstable rubbers are produced for long term applications at 180–200°C, for

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limited term applications at 250°C and for short term applications at 300°C.

But the rubbers on the basis of PDMS elastomers rapidly age in consequence of thermal-oxidative destructive processes. Besides of the thermal-oxidative destruction of linear PDMS elastomers the breaks of the Si—C and Si—O—Si bonds also occur.

The break of Si—C bonds proceeds with radical mechanism and Si—O—Si depends on the flexibility of chain at the availability of two surrounding organic groups at the silicon atom. Vulcanization of a linear dimethylsiloxane links by using vulcanizative agents in the process of obtaining rubbers, considerably reduces break Si—O—Si chain, but does not remove it. Therefore to increase the thermal stability of elastomers, especially working at a high temperature (> 250°C) it is necessary not only to protect the surrounding groups from radical processes, but also stabilize the main chain of macromolecules. Consequently, one of the most useful methods of obtaining the siliconorganic polymers, combining a high thermal-oxidative stability with flexibility, is a modification and stabilization of linear PDMS.

For stabilization of a main chain of macromolecules it is necessary to elaborate methods of synthesis such siliconorganic copolymers which consists of flexible linear dimethylsiloxane fragments and rigid mono-, bi- and polycyclic fragments both in the main and in the side chain.

Dimethylsiloxane copolymers with cyclic fragments in the side chain may be obtained not only by the reaction of polymerization of bisorganocyclosiloxaneoxides and α, ω -bisorganocyclosiloxymethylsiloxanes but also by heterofunctional condensations.

It must be denote that heterofunctional condensation reactions modification of functional group, containing methylsiloxanes with monofunctional organocyclosiloxanes [1], or heterofunctional polycondensations of dichloroorganosiloxymethylorganocyclosiloxanes with α, ω -dihydroxydimethylsiloxanes [2] have been previously reported.

It was also shown that the insertion of cyclic fragments in the side chain increases the thermal-oxidative stability of copolymers and the main destruction process proceeds about 80–100°C higher (in the case of phenylcyclosiloxane fragments in the side chain) than the destruction of unblocked PDMS.

Before our investigations there was no information in literature about dimethylsiloxane copolymers where in a silicon atom, instead of linear dimethylsiloxane links, or cyclic fragments there are bis(organo-cyclosiloxy) fragments.

EXPERIMENTAL PART

The organic solvents were purified by drying and distillation.

The purity of all initial organochlorosilanes and siloxanes have been controlled by their boiling temperatures, chlorine ions content, hydroxy group content and refraction indexes.

The initial α, ω -dihydroxydimethylsiloxanes [1] and hydroxyorgano-cyclosiloxanes have been synthesized by well-known methods [3, 4].

IR spectra of all the samples have been taken on an UR-20 instrument, while the ^1H NMR spectra on a "Perkin-Elmer" R-32 at operating frequency of 90 MHz in the solutions of CCl_4 and dioxane HMDS or TMS as internal standard.

The purity of obtained chlorine containing organocyclosiloxane was verified on a gas-liquid chromatograph "XM-8M Δ " phase SKTF-100 (10%), the NAW chromosorb, carrier gas-He, the 2M column.

Diffractionograms were taken on a " $\Delta\text{POH-2}$ " instrument, A-CU_a, the values were measured without a filter, the angular velocity of the motor $\omega = 2$ deg/min.

The thermomechanical curves were taken on a custom made installation. The test conditions were: $V = 5$ deg/min, $\delta = 0,1$ kg/cm².

Thermogravimetric investigations were carried out on a "Paulic-Paulic-Erdey" derivatograph, model MOM-102. The conditions of test were: temperature rise rate $V = 5$ deg/min, weight $m = 100$ mg.

Heterofunctional Condensation

of Hydroxypentaphenylcyclotrisiloxane with Tetrachlorosilane

The condensation reaction was carried out in a four-necked flask equipped with a reflux condenser and chlorocalcium tube, dropping funnel and mechanical stirrer. To the solution of 15,80 g (0,1000 mole) of tetrachlorosilane in 100 ml of anhydrous toluene at $-5 \div 0^\circ\text{C}$ simultaneously was added the solution of 25,00 g (0,0500 mole) hydroxypentaphenyltrisiloxane in 200 ml of anhydrous toluene and

the solution of 3,70 g (0,0500 mole) pyridin in 30 ml of anhydrous toluene.

The reaction mixture was stirred and heated up to boiling temperature of toluene for 3–4 hours. The residue was filtered off, the solvent was evaporated and 34,00 g of a product in vacuo 8,5 g (25%) of pure product I was isolated with $T_{\text{boil}} = 250–252^{\circ}\text{C}$, $P = 1–2 \times 10^{-2}$ mm Hg, $T_{\text{melt}} = 57–58^{\circ}\text{C}$, IR bands: 1000, 1435 (SiPh), 1020 (SiOSi), 2900–3000 (CH), 470, 560 (SiCl).

Calculated for $\text{C}_{30}\text{H}_{25}\text{Cl}_3\text{Si}_4\text{O}_4$ % : C 53,93; H 3,75; Cl 15,95; Si 16,78; $M_w = 667$; Found % : C 53,62; H 3,81; Cl 14,84; Si 16,42; $M = 630$; in addition 14,3 g (42%) of product III was isolated with $T_{\text{boil}} = 320–322^{\circ}\text{C}$ $P = 1–2 \times 10^2$ mm Hg. $T_{\text{melt}} = 59–60^{\circ}\text{C}$, IR bands 1000, 1435 (SiPh), 1020 (SiOSi), 2900–3000 (CH), 470, 560 (SiCl) Calculated for $\text{C}_{60}\text{H}_{50}\text{Cl}_2\text{Si}_7\text{O}_8$ %: C 61,82; H 4,29; Cl 6,09; Si 16,82; $M = 1165$; Found %: C 61,69; H 4,11; Cl 5,81; Si 16,48; $M = 1120$, and 11,2 g high boiling point products.

Heterofunctional Condensation of Hydroxyheptamethylcyclotetrasiloxane with Tetrachlorosilane

To the solution of 68,20 g (0,4000 mole) of tetrachlorosilane in 100 ml of anhydrous at $-5 \div 0^{\circ}\text{C}$ temperature simultaneously was added the solution of 60,0 g (0,2000 mole) hydroxyheptamethylcyclotetrasiloxane in 200 ml anhydrous ether and the solution of 20,30 g (0,2000 mole) triethylamine in 30 ml of anhydrous ether. The reaction mixture was stirred and heated at reflux for 3–4 hours. The residue was filtered off, the solvent was evaporated and 82,0 g of viscous product was obtained. After distillation of 82,0 g of product in vacuo 18,0 g (22%) of pure product II was isolated with $T_{\text{boil}} = 56–57^{\circ}\text{C}$, $P = 2 \times 10^{-1}$ mmHg. IR bands: 1275 (SiMe); 1080 (SiOSi), 470, 560 (SiCl).

Calculated for $\text{C}_7\text{H}_{21}\text{Cl}_3\text{Si}_5\text{O}_5$ %: C 19,47; H 4,87; Cl 24,68; Si 32,44; $M_{\text{RD}} = 93,2$, $M = 431$.

Found %: C 19,35; H 4,68; Cl 24,21; Si 32,30; $M_{\text{RD}} = 92,5$, $M = 410$ and 36,9 (45%) product IY was isolated with $T_{\text{boil}} = 115–118^{\circ}\text{C}$, $P = 2 \times 10^{-1}$ mmHg. IR bands: 1275 (SiMe); 1080 (SiOSi), 470, 560(SiCl).

Calculated for $\text{C}_{14}\text{H}_{42}$, Cl_2 , Si_9O_{10} %: C 24,24; H 6,06; Cl 10,24; Si 36,36; $M_{\text{RD}} = 157,2$, $M = 693$.

Found %; C 24,10; H 5,98; Cl 10,80; Si 36,32; $M_{RD} = 156,4$, $M = 700$, and 27.1 g high boiling point products.

**Heterofunctional Condensation
of Bis(pentaphenylcyclotrisiloxy)dichlorosilane
with 1,5-dihydroxypentaphenyltrisiloxane**

To the solution of 15 g (0,0128 mole) bis(pentaphenylcyclotrisiloxy)dichlorosilane in 300 ml anhydrous toluene at $-5 \div -10^\circ\text{C}$ temperature we added the solution of 3,09 g (0,0128 mole) 1,5-dihydroxyhexamethyltrisiloxane and 2,50 g (0,0128 mole) anilin in 100 ml anhydrous toluene. The reaction mixture was stirred and heated up to boiling point of toluene for 3–4 hours. After that the residue was filtered off, the solvent was evaporated and 14,4 g viscous product was obtained. After recrystallization of 14,4 g product from toluene solution by heptan, 5,30 g (37%) of pure product XIV was isolated with $T_{\text{melt}} = 147 - 149^\circ\text{C}$. IR bands: 1275 (SiMe); 1000, 1435 (SiPh), 1020, 1080 (SiOSi), 2900–3000 (CH).

Calculated for $\text{C}_{66}\text{H}_{68}\text{Si}_{10}\text{O}_{12}$ % C 59,46; H 5,10, Si 21,02; $M = 1332$.
Found % : C 59,12; H 4,93; Si 21,27; $M = 1270$.

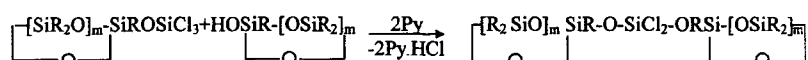
**Heterofunctional Polycondensation
of Bis(pentaphenylcyclotrisiloxy)dichlorosilane
with 1,3-dihydroxytetramethyldisiloxane**

The polycondensation reaction was carried out in a three-necked flask equipped with a reflux condenser, dropping funnel and mechanical stirrer. To the solution of 2,0141 g (0,0017 mole) bis(pentaphenylcyclotetrasiloxo)dichlorosilane II in 2 ml of anhydrous toluene at room temperature the solution of 0,2855 g (0,0017 mole) 1,3-dihydroxytetramethyldisiloxane and 0,2707 g (0,0034 mole) pyridin in 0,5 ml anhydrous toluene was added. The mixture was stirred and heated up to boiling temperature of toluene for 4–5 hours. After that, 8 ml of toluene was added, filtered and the reaction mixture was washed from the traces of pyridin hydrochloric acid, dried above anhydrous Na_2SO_4 and reprecipitated by using methyl alcohol.

The other typical reactions of syntheses of copolymers were carried out by above-mentioned method.

trasiloxane fragments accordingly. One can also observe absorption bands for Si—Me, Si—Ph and Si—Cl bonds in the region 1275, 1435 and 460, 570 cm^{-1} respectively.

Bis(organo-cyclosiloxy)dichlorosilanes have been synthesized also by the reaction of HFC of compounds (I, II) with hydroxyorgano-cyclosiloxanes in the 1:1 ratio of initial products in the temperature region $-5 \div -10^\circ\text{C}$ in presence of pyridin, according to the following scheme:



where $m = 2$, R = Ph(III), $m = 3$, R = Me(IV)

The synthesized compound III and IV were characterized by means of functional and elementary analysis by finding of molecular masses, by IR and ^1H NMR spectra.

The synthesis of the linear organosiloxane copolymers with the regular arrangement of bicyclosiloxane fragments in the side chain was carried out by the reaction of HFC of synthesized bis(organo-cyclosiloxy)dichlorosilanes with α, ω -dihydroxydimethylsiloxanes in the presence of pyridin. The reaction was carried out at room temperature, at the completing stage, the reaction mixture was heated for 4–5 hours. At small lengths of the linear dimethylsiloxane link the copolymers yield was low.

When HFC of bis(pentaphenylcyclo-trisiloxy)dichlorosilanes III with 1,5-dihydroxyhexamethyltrisiloxane was studied, after the polymer reprecipitation from the mother solution a low molecular product was obtained, which according to its composition and structure corresponds to a tricyclic compound. Consequently, the above-mentioned reaction of HFC proceeds to the following scheme:

Where $m = 1$, R = Ph: $n = 2$ (V), 3(VI), 4(VII), 8(VIII), 34(IX), 51(X); $m = 2$, R = Me: $n = 1$ (XI), 2(XII), 3(XIII)

The copolymers depending on surrounding fragments at silicon in the side chain are transparent or slightly opalescent substances, soluble in ordinary organic solvents with $\eta_{\text{spec}} = 0,03 \div 0,31$. The yield of obtained copolymers is 70–93%. Some physical–chemical properties, elementary analysis and yield of copolymers listed in Table I. As it is shown from data of Table I at a small length of the dimethylsiloxane

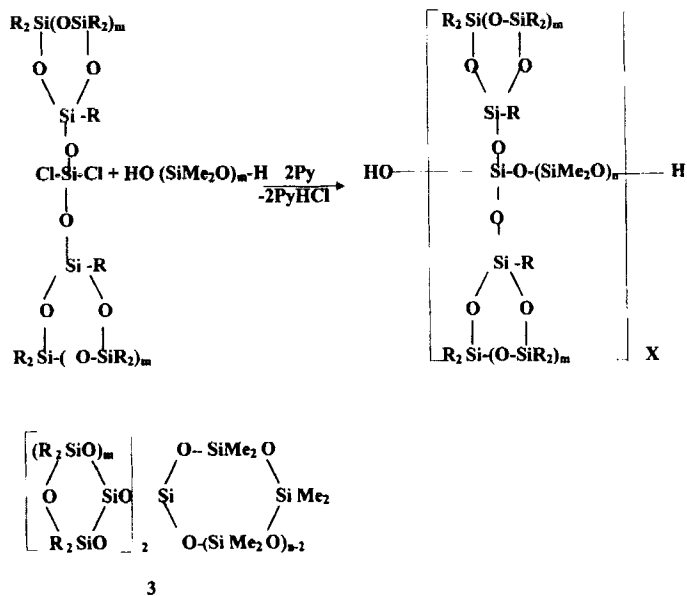


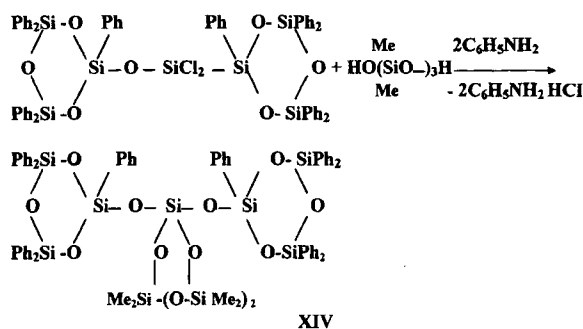
TABLE I Some physical-chemical properties and yields of bicyclic containing copolymers

Copolymer	yield, %	$T_{\text{vit.}}, ^\circ\text{C}$	$d_1, \text{\AA}$	$\eta_{\text{spec}}^\dagger$	Elementary composition, % [‡]		
					C	H	Si
V	73	+25	11,26	0,09	62,97	5,03	21,03
VI	72	-	-	0,11	63,16	5,26	20,72
					59,21	4,97	21,47
VII	81	+5	11,05	0,14	59,46	5,10	21,02
					58,12	5,11	21,43
VIII	88	-12	-	0,19	58,04	5,26	21,91
					52,97	5,40	24,15
IX	92	-90	-	0,28	53,16	5,76	24,67
					42,00	6,78	31,07
X	94	-123	-	0,31	42,36	7,00	31,66
					39,28	7,31	33,07
XI	83	-85	9,26	0,04	39,65	7,29	33,25
					26,80	6,50	39,11
XII	77	-90	-	0,05	26,96	6,74	39,32
					27,40	6,60	39,30
XIII	78	-95	9,12	0,07	27,48	6,87	39,28
					27,69	6,77	39,00
					27,90	6,98	39,07

[†]In toluene at 25°C. [‡]In the numerator there are experimental values and in the denominator-calculated values.

links ($n = 2 \div 4$) the yield of copolymers is a bit lower. This may be explained by the fact, that besides of formation of copolymers the reaction of HFC runs by intramolecular cyclization with formation of tricyclic compounds with the structure 3 (about $\sim 8-10\%$). After reprecipitation of synthesized copolymer VI from toluene solution by methylalcohol from the mother solution and after the removal of solvents we obtained the product with structure 3. The molecular weight of this product was about ~ 400 . This molecular weight corresponds only to products of intramolecular cyclization. For this product we determined the molecular masses, IR and NMR spectra. On the basis of such results the tricyclic structure of this product, was confirmed.

Such tricyclic structure product was obtained directly, by HFC of bis(pentaphenylcyclotrisiloxy)dichlorosilane with 1,5-dihydroxyhexamethyltrisiloxane with a 1:1 ratio of initial components in the presence of anilin at $-5 \div -10^\circ\text{C}$ temperature according to the following scheme:



This reaction leads to a solid product, which after recrystallization of from toluene solution by heptan yields 37% of a white powder like product. The composition and structure of the compound XIV was determined by means of elementary analysis, by finding molecular masses, IR and NMR spectra. In the IR spectra of compound XIV one can see the absorption bands for asymmetric valence oscillation of the Si—O—Si bonds in the region 1020 and 1080 cm^{-1} .

One can see also the absorption bands for Si—Ph, and Si—Me bonds at 1000 , 1445 and 1275 cm^{-1} accordingly.

In the ^1H NMR spectra of compound XIV one can observe the singlet signals for methyl groups with chemical shift $\delta = 0,12$ ppm, $\delta = 0,14$ and $\delta = 0,16$ ppm, and a complicated multiplet is observed in the 6,8–7,6 ppm region.

In the IR spectra of obtained copolymers in the region 1000–1100 cm^{-1} characteristic for asymmetric valence oscillation of the Si—O—Si bonds, besides of the absorption band 1020 cm^{-1} , where we find the absorption bands for linear siloxane bonds associated with Si—O—Si bonds in phenylcyclotrisiloxane rings, one can see also the absorption bands of Si—O—Si bonds in cyclotetrasiloxane rings at 1080 cm^{-1} . In the IR spectra we observe also the absorption, bands for Si—Ph (for copolymers (V–X) and Si—Me bands at 1000, 1445 and 1275 cm^{-1} accordingly.

The fractionation of copolymer VIII was carried out by partial reprecipitation from toluene solution by methanol, four fractions were obtained. Elementary analyses of this fractions differ slightly from each other. All these showed that during HFC, the reaction of homofunctional condensation is improbable and copolymers with regular arrangement of bicyclic fragments in the side chain are obtained.

We carried out the thermogravimetric investigation of synthesized copolymers. In Figures 1–2 the thermogravimetric curves for the copolymers are presented. Figures 1–2 show that the copolymers are characterized by higher thermal-oxidative stability than the linear polydimethylsiloxanes. In case of low values of dimethylsiloxane chain n , the copolymers are characterized with higher thermal-oxidative stability. With an increase of the length of dimethylsiloxane chain the thermal-oxidative stability of copolymers decreases.

For phenyl containing copolymers 5% mass losses are observed in the temperature region 370–400°C, while for copolymers with bis(heptamethylcyclotetrasiloxane) fragments in the side chain 5% mass losses are observed at 250–270°C temperatures. The main destruction process proceeds over the range 450–600°C, and 270–500°C, and above 500–600°C the curves of mass losses do not change.

The comparison of thermal-oxidative stability of copolymers of bisorganocyclosiloxane fragments in the side chain with copolymers with monocyclic fragments in the side chain [2], showed that

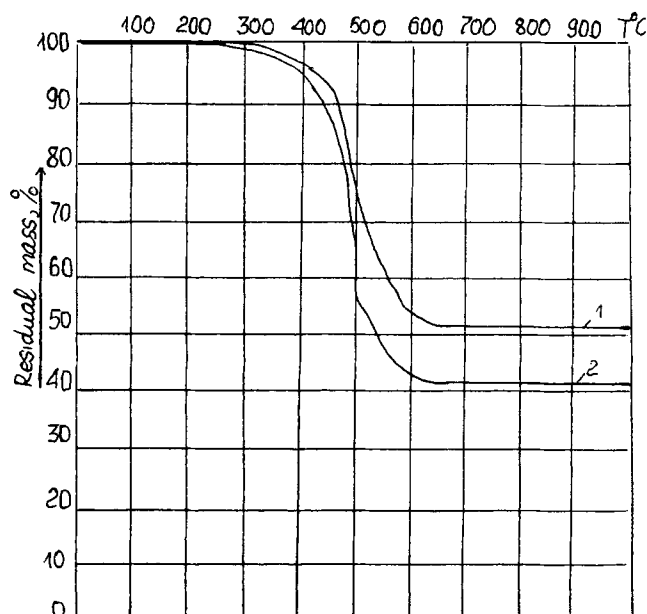


FIGURE 1 The thermogravimetric curves for copolymers with bis(pentaphenylcyclo-trisiloxane) fragments in the side chain, where curve 1 corresponds to copolymer V, curve 2 corresponds to copolymer VII.

bisorganocyclosiloxane fragments containing copolymers are more thermally stable.

The thermomechanical investigation of synthesized copolymers was carried out. As it is shown in Table I, T_{vitr} of copolymers bis(pentaphenylcyclo-trisiloxane) fragments in the side chain are characterized with higher T_{vitr} than copolymers with pentaphenylcyclo-trisiloxane fragments in the chain [2]. Replacement of one methyl group by pentaphenylcyclo-trisiloxane fragments in the silsesquioxane link leads to a rise in the vitrification temperature for about $\sim 30^\circ\text{C}$.

Copolymers with bisheptamethylcyclo-tetrasiloxane fragments in the side chain are characterized by lower value of vitrification temperature.

Replacement of a methyl group by heptamethylcyclo-tetrasiloxane fragments at the silsesquioxane link leads to a rise in vitrification temperature by 5°C . The increase of a linear dimethylsiloxane link by

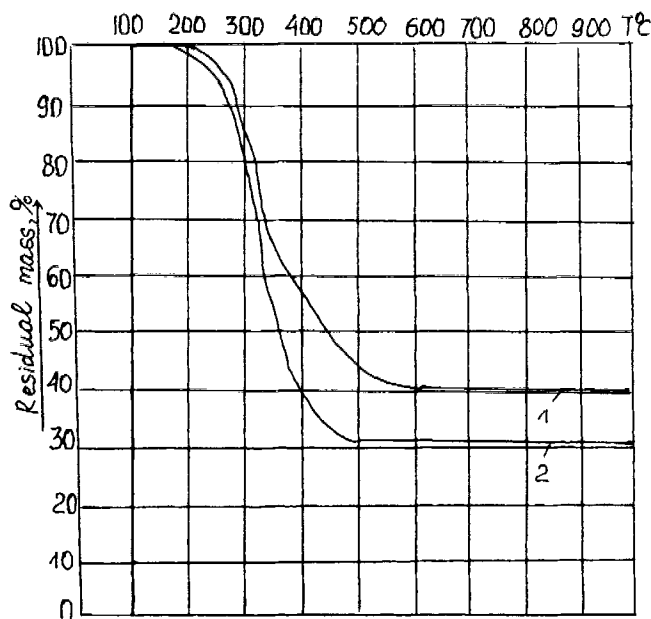


FIGURE 2 The thermogravimetric curves for copolymers with bisheptamethylcyclotetrasiloxane fragments in the side chain, where curve 1 corresponds to copolymer XI and curve 2 corresponds to copolymer XIII.

one dimethylsiloxo unit leads to a decrease of vitrification temperature by 5°C [2].

X-ray analysis of the synthesized copolymers showed that all copolymers are amorphous one phase systems with two diffraction maxima. As it is shown in Figure 3, the maximum value of interchain distance d_1 occurs with copolymers with bispentaphenylcyclotrisiloxane fragments in the side chain, and for copolymer V $d_1 = 11,26 \text{ \AA}$. With an increase of a length of dimethylsiloxane chain "n" the value of d_1 decreases and for copolymer VII $xd_1 = 11,05 \text{ \AA}$. For copolymer XIII with bisheptamethylcyclotetrasiloxane fragments in the side chain, the interchain distance $d_1 = 9,12 \text{ \AA}$.

The value of interchain distance for copolymers with bisheptaphenylcyclotrisiloxane fragments in the side chain approximately equals to interchain distance for cycloliner copolymers with phenylcyclohexasiloxane fragments in the main chain [5].

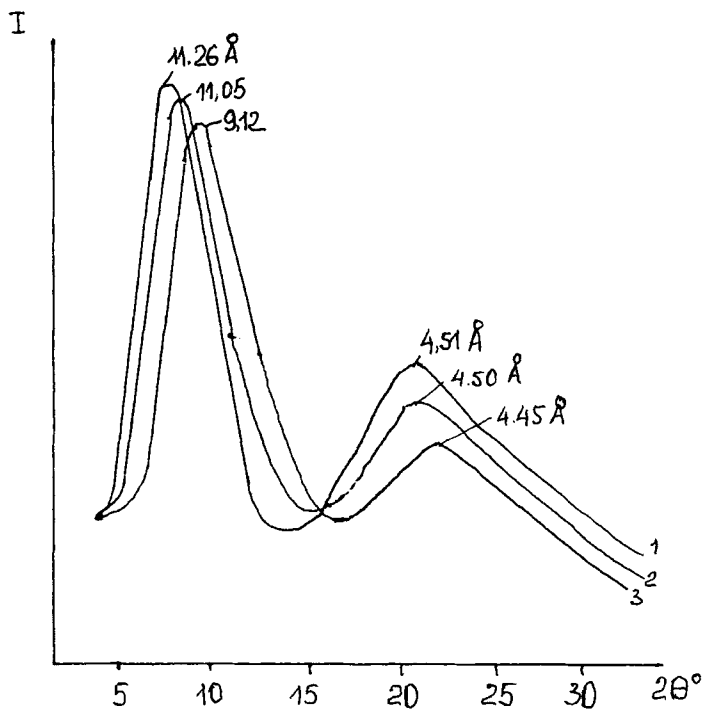


FIGURE 3 Diffractograms of copolymers, where curve 1 is for copolymer V, curve 2 corresponds to copolymer VII and curve 3 corresponds to copolymer XIII.I.

References

- [1] Mukbaniani, O. V., Khananashvili, L. M., Esartia, I. G., Khaduri, S. I. and Porchkidze, G. V. (1993). *Intern. J. Polymeric Materials*, **22**, 131–139.
- [2] Mukbaniani, O. V., Meladze, S. M., Esartia, I. G., Tverdokhlebova, I. I. and Khananashvili, L. M., *Intern. J. Polymeric Materials*, in press.
- [3] Sokolov Zhurn, N. N. (1959). *Obshch. Khim.*, **29**, 258.
- [4] Meladze, S. M. (1980). Synthesis and Investigation of the Properties of Organosiloxane Oligomers and Polymers of Cyclolinear and Spirocyclic Structure, *Cand. Dissertation. Tbilisi*, 99.
- [5] Meladze, S. M., Mukbaniani, O. V. and Khananashvili, L. M. (1984). *Vysokomol. Soed.*, **26B**, 250–253.