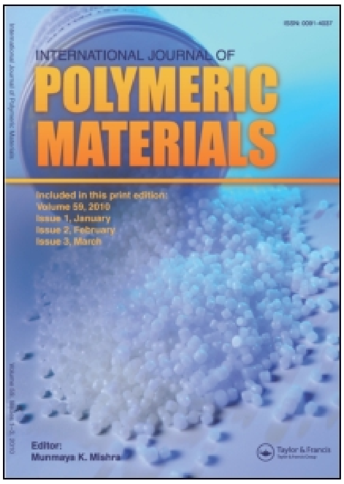

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Card-type Organosiloxane Copolymers with Silaoxaphenantrene Fragments in Dimethylsiloxane Chain

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The reaction of heterofunctional condensation of 1,1-dichloro-1-sila-2-oxaphenantrene with α,ω-dihydroxydimethylsiloxane in the presence of pyridine has been investigated and card-type organosiloxane copolymers with regular arrangement of silaoxaphenantrene fragments in dimethylsiloxane chain has been obtained. It is shown, that at small length of linear dimethylsiloxane chain, besides the reaction of intermolecular condensation, intramolecular cyclization takes place with formation of bicyclic compounds. Thermogravimetric, DSC, GPC and X-ray analysis of the synthesised copolymers have been carried out.

Keywords: Organosiloxane copolymers; Silaoxaphenantrene_fragments; Heterofunctional condensation

INTRODUCTION

From the literature it is known that linear polydimethylsiloxanes possess good elastic properties and are easily processible, but they have a comparatively low thermal oxidative stability. The unblocked

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*Corresponding author.

polydimethylsiloxane (PDMS) polymers are subject to full thermal-oxidative destruction at 230–250°C [1].

But from other literature sources [2, 3], it is known that the insertion in the linear polydimethylsiloxane chain of heteroatoms and of various cyclic fragments breaks the spyral structure of the copolymers and changes their physical–chemical properties.

Because of that, a most promising method of obtaining polymers which combine high thermal oxidative stability with elasticity is the modification of the linear PDMS. Cyclolinear organosiloxane copolymers with cyclic fragments in the main dimethylsiloxane chain has been obtained by heterofunctional condensation (HFC) of dichloro-(dihydroxy)organocyclosiloxanes with α,ω-dihydroxy(dichloro, bis-dimethylamino)dimethylsiloxanes [4].

Cyclolinear copolymers with monocyclic fragments in the side chain were synthesised by HFC of dichlorosiloxyorganocyclosiloxanes with α,ω-dihydroxydimethylsiloxanes in the presence of amines [5, 6].

Card-type cyclolinear copolymers were synthesised by HFC of dichloroorganocyclosiloxanes with α,ω-dihydroxydimethylsiloxanes in the presence of amines [7]. It was shown that during HFC, at small lengths of dimethylsiloxane chain, besides the intermolecular condensation, the reaction proceeds by intramolecular cyclization.

EXPERIMENTAL PART

The starting materials 1,1-dichloro-1-silaoxaphenantrene and α,ω-dihydroxydimethylsiloxanes with various length were synthesised by a well-known methods [8, 9].

The organic solvents were purified by drying and distillation. The purity of the starting compounds was controlled by gas–liquid chromatography "ЛХМ-8 МД", phase SKTF-100 (10%), the NAW chromosorb, carrier gas–He, with 2 M column.

IR spectra of synthesized compounds has been taken on an UR-20 instrument and ^{1}H NMR spectra on a Perkin-Elmer instrument at operating frequency of 250 MHz in solutions of $C_2D_2Cl_4$ or $CDCl_3$.

Diffractograms were taken on a "ДРОН-2" instrument, A-Cu_{α} values were measured without a filter, the angular velocity of the motor $\omega = 2$ deg/min.

The DSC analysis were carried out on a Perkin-Elmer instrument with temperature rise or decrease rate $\nu = 10$ deg/min. Thermogravimetric investigations were carried out on a "Paulic-Paulic Erdey" derivatograph, model MOM-102. The test conditions were: temperature rise rate $\nu = 5$ deg/min, in air.

Heterofunctional Condensation of 1,1-dichloro-2-oxaphenantrene with 1,3-dihydroxytetramethyldisiloxane (in Concentrated Solution)

The polycondensation reaction was carried out in a three-necked flask equipped with a reflux condenser, dropping funnel and mechanical stirrer. To a solution of 1,4730 g (5,516 mmole) 1,1-dichloro-1-sila-2-oxaphenantrene in 1 ml anhydrous toluene at room temperature a solution of 0,9157 g (5,516 mmole) 1,3-dihydroxytetramethyldisiloxane and 0,8728 g (11,033 mmole) pyridine in 0,5 ml anhydrous toluene was added. The mixture was stirred and heated up to the boiling temperature of toluene for 5 hours, after that, 8 ml of toluene was added, filtered and the reaction mixture was washed from the traces of pyridine–HCl complex, dried above anhydrous Na_2SO_4, part of toluene removed and reprecipitated by using methyl alcohol.

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

Heterofunctional Condensation of 1,1-dichloro-1-sila-2-oxaphenantrene with 1,3-dihydroxytetramethyldisiloxane (in Dilute Solution)

The reaction of heterofunctional condensation was carried out in a four-necked flask equipped with a reflux condenser, dropping funnels and mechanical stirrer. To a solution of 5,8920 g (22,064 mmole) 1,1-dichloro-1-sila-2-oxaphenantrene in 70 ml anhydrous ether at room temperature a solution of 3,6628 g (22,064 mmole) 1,3-dihydroxytetramethyldisiloxane in 30 ml anhydrous ether and 4,1042 g (44,132 mmole) aniline in 35 ml anhydrous ether was added. The mixture was stirred and heated for 4 h. After that the residue was filtered off and the reaction mixture washed from the traces of pyridine-HCl complex, dried above anhydrous Na_2SO_4, the solvent evaporated and 6,9 g viscous product was obtained. After distillation of the 6,9 g product in vacuo 2,4 g (34,8%) of pure product VII was isolated with $T_{boil} = 138-140°C$ ($P = 1-3 \times 10^{-1}$ mmHg), $T_{melt} = 34-36°C$, IR bands 1000,1435 (SiPh), 1020,1075 (SiOSi), 2900-3000 (CH), 1275 cm^{-1} (SiMe).

Calculated for $C_{16}H_{20}Si_3O_4$%: C 53,33; H 5,55; Si 23,33; $M = 360$.
Found %: C 52,95; H 5,26; Si 23,49; $M \approx 385$.

RESULTS AND DISCUSSION

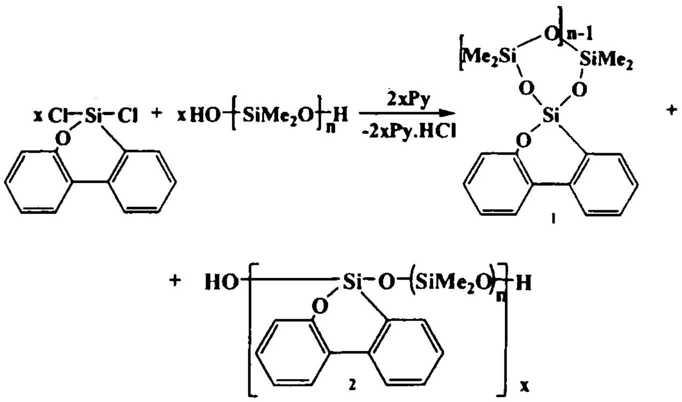
In the literature there is no information about card-type organosiloxane copolymers with the regular arrangement of silaoxaphenantrene fragments in the dimethyloxane chain.

For the purpose of synthesis of card-type cyclolinear copolymers, the reaction of HFC of 1,1-dichloro-1-sila-2-oxaphenantrene with α,ω-dihydroxydimethylsiloxane with various length of siloxane chain, at 1 : 1 ratio of initial compounds in the presence of pyridine, as an acceptor of hydrogen chloride, was investigated. As is known, the use of the acceptor leads to increasing efficiency of HFC [10]. The reaction was carried out at room temperature, at the completing stage the reaction mixture heated up to the boiling point of the solvent used.

The secondary reactions of homofunctional condensations of α,ω-dihydroxydimethylsiloxanes does not take place in such conditions. Earlier it was shown by the authors [11] that homofunctional condensation 1,3-dihydroxytetramethyldisiloxane does not take place in the presence of amines more basic than pyridine.

At a small length of the linear dimethylsiloxane segment ($n \leq 4$) the copolymers yield is low, which may be explained by the fact, that besides the intermolecular condensation, there partially takes place an intramolecular cyclization, with the formation of cyclic compounds.

These two paths of HFC during synthesis of cyclolinear copolymers were early suggested by us [6, 7]. The reaction proceeds according to the following scheme:



SCHEME

Where: $n = 2$(I), 4(II), 8(III), 12(IV), 19(V), 27(VI).

The synthesised copolymers with structure 2 were reprecipitated from toluene solution with methyl alcohol. The yield of the obtained copolymers is $73 \div 95\%$. Depending on the length of linear dimethylsiloxane chain the copolymers are transparent or slightly opalescent substances, soluble in ordinary organic solvents, with $\eta_{sp} = 0,11 \div 2,33$. Some physical-chemical properties, elementary analysis and yield of copolymers listed in Table I.

As is seen from the structure of 1,1-dichloro-1-sila-2-oxaphenantrene, it contains six member heterocyclic fragment with Si—O—C bond. From literature it is known that ordinary Si—O—C bond is easily cleaved by basic and acid reagents, and Si—C_{aryl} bond is especially sensitive to action of acids [12]. But it was shown by the authors [12] that 1,1-dichloro-1-sila-2-oxaphenantrene is not destroyed during boiling with water, with alkali-alcohol solution and with concentrated hydrogen chloride. It was shown that alkylation and arylation with Grinard reagents, restoration with $LiAlH_4$ and processing with hydrogen Fluoride do not break Si—O—C bonds.

TABLE I Physical–chemical properties and yields of silaoxaphenantrene-dimethylsiloxane copolymers

Copolymer, $	*Yield,* %	T_g, °*C*	d_1, *Å*	$[\eta]^{*}$	*5%-mass losse*	$\overline{M}_w \times 10^{-3}$	*Elementary composition,*[1] % *C*	*H*	*Si*
I	73	0	9,30	0,11	350	–	$\frac{53,33}{52,84}$	$\frac{5,56}{4,96}$	$\frac{23,33}{23,11}$
II	86	−32	8,23	0,15	300	150	$\frac{47,24}{46,85}$	$\frac{6,30}{6,42}$	$\frac{27,56}{27,41}$
III	93	−62	–	0,28	–	–	$\frac{41,79}{41,35}$	$\frac{6,97}{6,80}$	$\frac{31,34}{31,45}$
IV	94	−85	–	0,40	–	–	$\frac{39,27}{38,87}$	$\frac{7,27}{6,86}$	$\frac{33,10}{32,79}$
IV^1	16	–	–	0,61	–	–	$\frac{39,27}{39,10}$	$\frac{7,27}{6,80}$	$\frac{33,10}{32,87}$
IV^2	21	–	–	0,48	–	–	$\frac{39,27}{38,70}$	$\frac{7,27}{7,00}$	$\frac{33,10}{32,64}$
IV^3	27	–	–	0,35	–	–	$\frac{39,27}{38,96}$	$\frac{7,27}{6,61}$	$\frac{33,10}{32,90}$
IV^4	36	–	–	0,30	–	–	$\frac{39,27}{38,81}$	$\frac{7,27}{6,95}$	$\frac{33,10}{32,94}$
V	95	−112	7,50	1,82	350	387	$\frac{37,08}{36,70}$	$\frac{7,54}{7,35}$	$\frac{34,61}{34,23}$
VI	94	−123	7,37	2,33	300	648	$\frac{35,84}{36,01}$	$\frac{7,69}{7,53}$	$\frac{35,48}{35,11}$

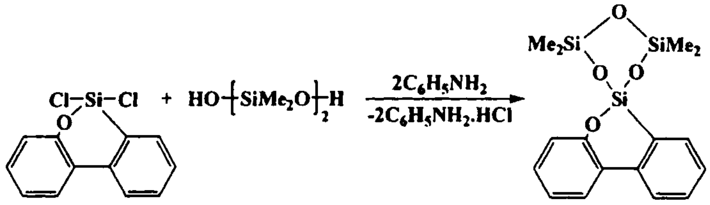
* In toluene at 25°C.

[1] In numerator there are calculated values, and in denominator-experimental values.

High chemical stability of silaoxaphenantrene fragments indicates a definite degree of aromaticity of this compound [13].

During reprecipitation of copolymer I from the mother solution of toluene and by methyl alcohol, and after removal of solvents a low-molecular weight product was obtained at ~6% yield, which according to its composition and structure correspond to the bicyclic structure 1. For this product molecular masses, IR and NMR spectra were determined, and from this the cyclic structure of compounds with structure 1 was proved. Such product of cyclic structure 1 ($n = 2$) was obtained by HFC of 1,1-dichloro-1-sila-2-oxaphenantrene with 1,3-dihydroxytetramethyldisiloxane with 1 : 1 ratio of the initial compounds in the presence of aniline in 5% solution of anhydrous ether. After distillation of the reaction products bicyclic compound VII with the structure 1 has been obtained.

The reaction proceeds according to the following scheme:



SCHEME

Where: $n=2$ (VII).

The composition and structure of compound VII were determined by means of element analysis, by finding the molecular masses, by IR and ^{1}H NMR spectra data. In the IR spectrum of compound VII one can see the absorption band for asymmetric valence oscillation of Si—O—Si bonds in the region 1020 and 1075 cm^{-1}. One can see also the absorption bands for Si—Me and Si—Ph bonds at 1275 and 1435 cm^{-1} respectively.

In the ^{1}H NMR spectra of compound VII one can see the singlet signal for methyl protons with chemical shift $\delta=0{,}14$ ppm, and a complicated multiplet for phenyl protons in the range $6{,}7 \div 7{,}5$ ppm, integral intensity of the signals corresponds to the expectation from structure VII.

Copolymer IV was fractionated to four fractions ($IV^1 \div IV^4$). As is seen from Table I element analysis of the copolymers showed slight difference among them. Which proved that during HFC secondary processess do not take place.

GPC investigation of the copolymers has been carried out. In Figure 1 the molecular weight distributions (MWD) of the copolymers are presented. As is seen from Figure 1 the MWD of the copolymers is monomodal. The average molecular weights $\overline{M}_w$ of copolymers are in the range $1{,}5 \times 10^5 \div 5{,}0 \times 10^5$ and the polydispersity of copolymers lies in the range $2{,}0 \div 3{,}0$. The values of molecular masses ($\overline{M}_w$, $\overline{M}_n$) and polydispersity are presented in Table I.

DSC analysis of the synthesised copolymer has been carried out. As is seen from Figure 2 the maximum value of the glass temperature

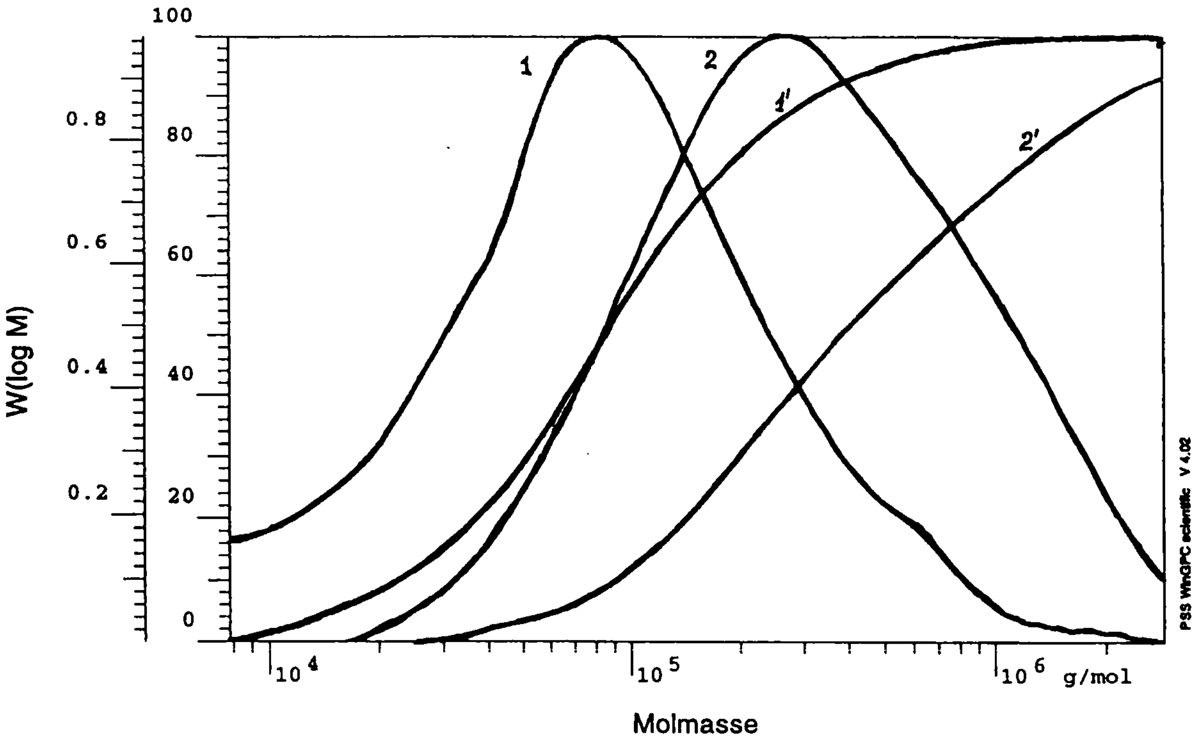


FIGURE 1 Molecular weight distribution of card-type copolymers. Where curves 1,1'-correspond to copolymer I, curves 2,2' correspond to copolymer V.

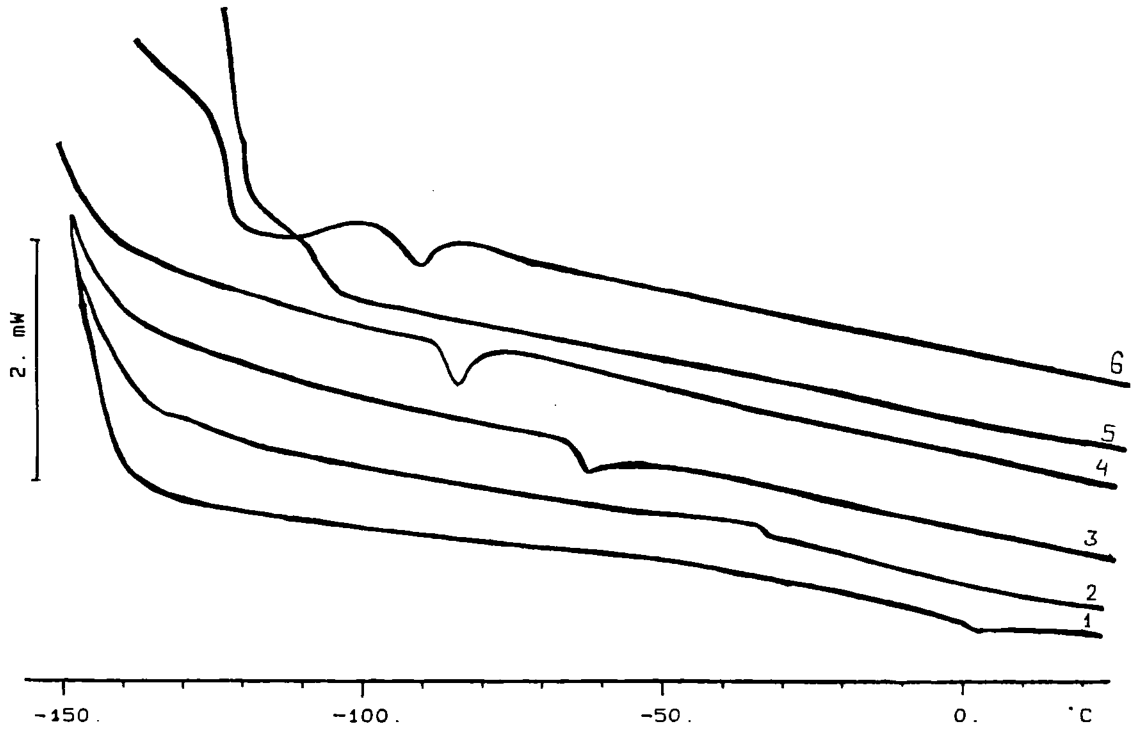


FIGURE 2 DSC curves of silaoxaphenantrene-dimethylsiloxane copolymers. Where curve 1 corresponds to copolymer I, 2-II, 3-III, 4-IV, 5-V, 6-VI.

T_g of the copolymers is reached at short lengths of the linear polydimethylsiloxane chain. In Figure 3 the dependence of T_g on the length of linear dimethylsiloxane chain is presented, from which it is evident that, with an increase of the length of dimethylsiloxane chain, the T_g of the copolymers decreases towards the T_g of the linear polydimethylsiloxane. The influence of 1-sila-2-oxaphenantrene fragment on the length of dimethylsiloxane chain is detectable until $n \approx 19$, in this case T_g of copolymer V is equal to $-112°C$.

The copolymers are single phase amorphous system and maximum values of interchain distances d_1 is observed for short dimethylsiloxane chains and for copolymer I $d_1 = 9{,}30$ Å, this value of d_1 approximately equals to d_1 characteristic for cyclolinear copolymers with organocyclopenta siloxane and organocyclohexasiloxane fragments in the main dimethylsiloxane chain [14]. As is seen from Figure 4, with an increase in the length of the dimethylsiloxane chain "*n*", the value of d_1 decreases and for copolymer VI $d_1 = 7{,}37$ Å, this value of interchain distances equals the d_1 characteristic for linear PDMS.

Thermogravimetric investigation of the copolymers has been carried out. In Figure 5 the thermogravimetric curves of the copolymers are presented. The copolymers with short dimethylsiloxane chains are characterized by higher thermal-oxidative stability (curves

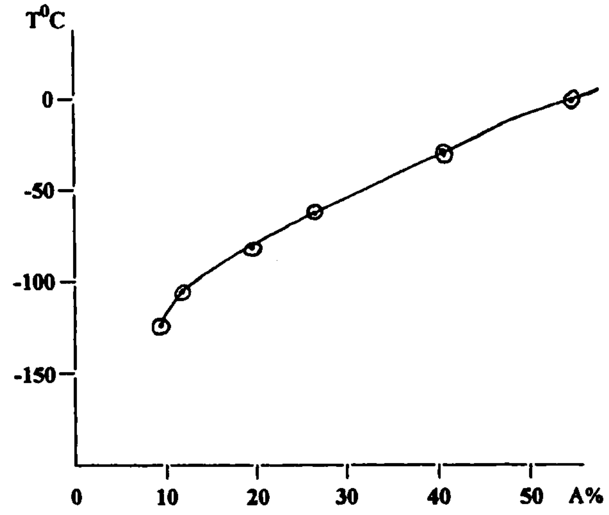


FIGURE 3 Dependence of T_g on mole% content of silaoxaphenantrene (A) fragments.

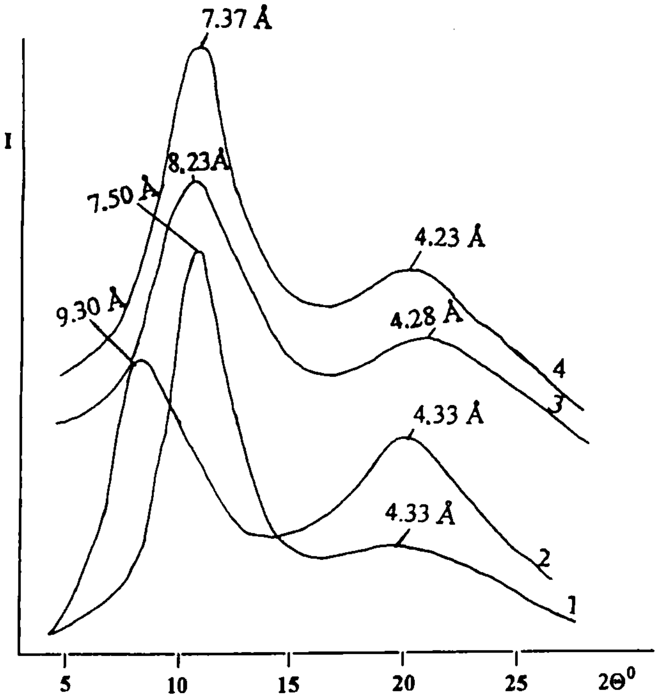


FIGURE 4 Diffractograms of copolymers. Where curve 1 is for copolymer V, 2-I, 3-II and 4-VI.

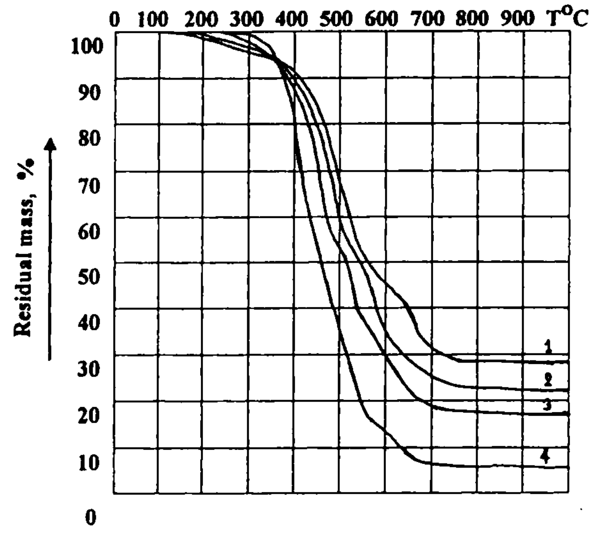


FIGURE 5 Thermogravimetric curves for copolymers with silaoxaphenantrene fragments in dimethylsiloxane chain. Where curve 1 corresponds to copolymer I, curve 2-II, 3-V and 4-VI.

1 and 2). As the length of dimethylsiloxane chain increases, the thermal-oxidative stability of the copolymers decreases.

5% mass losses for the copolymers were observed in the temperature range 300 ÷ 350°C, the main destruction process proceeds in the 450 ÷ 700°C temperature range and above 700°C the curves of mass losses do not change. So, with the insertion of 1-sila-2-oxaphenantrene fragment in dimethylsiloxane chain the main process of thermal-oxidative destruction starts about 100°C higher compared with the linear PDMS [1].

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