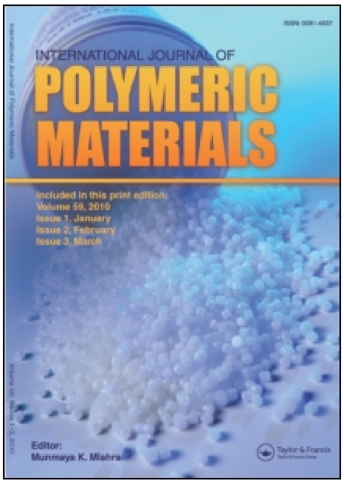

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Silarylencyclohexasiloxane – Polydimethylsiloxane Block-copolymers

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The reaction of heterofunctional condensation of 1,7-dihydroxy-1,7-dimethyloctaphenylcyclohexasiloxane with 1,4-bis(dimethylchlorsilyl)benzene in the presence of pyridin with 1:0.95 and 1:1 ratio of initial components have been investigated and α,ω-dihydroxysilarylencyclohexasiloxane oligomers have been obtained. On the basis of synthesized oligomers the corresponding block-copolymers were obtained by the reaction of heterofunctional condensation with α,ω-dichlordimethylsiloxanes. Thermomechanical, thermogravimetric and X-ray studies of block-copolymers show that their properties are determined by a ratio of the lengths of flexible linear dimethylsiloxane and rigid silarylen-chclohexasiloxane fragments in the chain. When the lengths of the linear dimethylsiloxane fragments have definite values, the microheterogeneous structure is observed in synthesized block-copolymers.

Keywords: Heterofunctional condensation; organosilicon block-copolymers; thermal-oxidative stability

INTRODUCTION

The organosilicon block-copolymers have recently received widespread attention [1]. There is information about siliconorganic block-copolymers with cyclolinear structure of macromolecules. From A_mB_n type block-copolymers the block-copolymers with bead-like structure

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[2], block-copolymers with organotetracylosiloxane and ladder polyphenylsiloxanes with single and double stranded fragments in dimethylsiloxane chain [3, 4], were obtained.

Occurrence of block-structure (phase incompatibility) in copolymers must be connected with the value *m* and *n* of rigid and flexible fragments. In the copolymers consisting of dimethylsiloxane and cyclosiloxane blocks [3], the value of *n* for dimethylsiloxane blocks, from which flexible block properties start to appear, must be higher than 20, while polycyclic (ladder) blocks even with $m = 3 \div 5$ exhibit properties characteristic for rigid block systems. Therefore, at certain values of *m* and *n* segregation processes take place resulting in formation of domains containing rigid and flexible blocks.

EXPERIMENTAL PART

The organic solvents were purified by drying and distillation. The initial 1,7-dihydroxy-1,7-dimethyloctaphenylcyclohexasiloxane and 1,4-bis(dimethylsilyl)benzene were synthesized by well-known methods [5, 6].

The IR spectra of all the sample were taken on a UR-20 spectrophotometer. The purity of initial components were verified on a gas-liquid chromatograph "UXW-8MD" (USSR). Phase SKTF-100 (10%) on the NAW chromosorb, carrier gas – helium, on the 2 M column.

Diffractograms were taken on a "DPOH-2" instrument, A – Cuα, were measured without a filter, the angular velocity of motor $\omega = 2$ deg/min.

The thermomechanical curves were taken on a custom-made installation. The test conditions were: $\nu = 5$ deg/min, $\sigma = 0.1$ kg/cm^2.

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

Heterofunctional Polycondensation of 1,7-Dihydroxy-1,7-Dimethyloctaphenylcyclohexasiloxane with 1,4-bis(Dimethylchlosilyl)Benzene

The reaction of HFC was carried out in a three-necked flask equipped with a reflux condenser, dropping funnel and mechanical stirrer. To the solution of 1.37 g (0.0167 mole) in 5 ml unhydrous benzene at temperature 20–25°C the solution of 16.7000 g (0.0175 mole) 1,7-dihydroxy-1,7-dimethyloctaphenylcyclohexasiloxane 2.83 ml (0.0175 mole) pyridin in 10 ml of unhydrous benzene was added. The reaction mixture was stirred and heated up to boiling temperature of benzene during 4–5 hours. After that 8 ml of benzene was added filtrated and the reaction mixture was washed from traces of pyridin-hydrochloric acid, dried above anhydrous Na_2SO_4, and, after removal of benzene was reprecipitated by using methanole. It was obtained 15 g (80%) oligomer I.

The typical reaction of synthesis of oligomer II was carried out by above mentioned method with the ratio of initial components 1:1.

Heterofunctional Polycondensation of α,ω-Dihydroxysilarylencyclohexasiloxane Oligomer I with 1,3-Dichlortetramethyldisiloxane

To the solution of 0.1787 g (8.8029×10^{-2} mole) 1,3-dichlortetramethyldisiloxane in 0.5 ml of anhydrous toluene at room temperature the solution of 4.0088 (8.8029×10^{-2} mole) α,ω-dihydroxysilarylencyclohexasiloxane oligomer, 0.14 ml (1.7606×10^{-2} mole) pyridin in 1,5 ml anhydrous toluene was added.

The mixture was stirred and heated up to boiling temperature of toluene during 4 hours. Then the reaction mixture was diluted with 5 ml toluene, filtrated and washed from the traces of pyridin hydrochloric acid, dried above anhydrous Na SO and reprecipitated from the toluene solution by methanole 3.8 g (93%) of copolymer III was obtained.

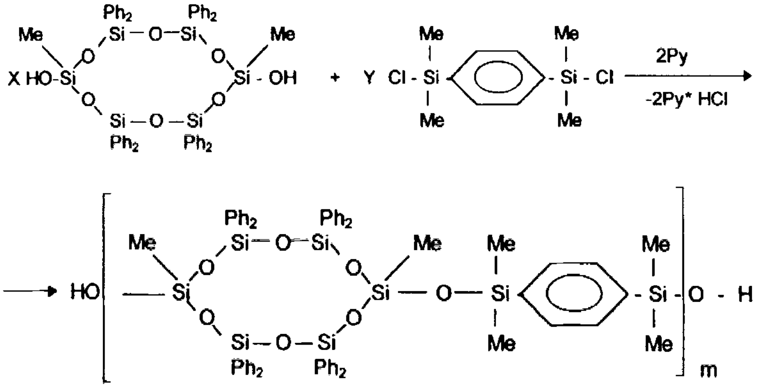
The other typical reactions of syntheses of block-copolymers were carried out by above mentioned method.

RESULTS AND DISCUSSION

In literature there is little information about silarylencyclosiloxane oligomers and corresponding $(AB)_mC_n$ type block-copolymers [7]. One of the most important methods of receiving of such block-copolymers is the reaction of HFC.

For purpose of sytheses $(AB)_mC_n$ type block-copolymers, which contain in macromolecular chain at the same time with linear dimethylsiloxane chain, silarylencyclohexasiloxane fragments in the capacity of initial product was used α,ω-dihydroxysilarylencyclohexasiloxanes.

For synthesis of the α,ω-dihydroxysilarylencyclohexasiloxanes with the various depth of condensation it was carried out the reaction of HFC of 1,7-dihydroxy-1,7-dimethyloctaphenylcyclohexasiloxane with 1,4-bis(dimethylchlosily)benzene by ratio of initial components 1:0.95 and 1:1 at 20–25°C temperature, in toluene solution in the presence of pyridin. At the completing stage the reaction mixture heated up to boiling point of using toluene. The reaction of HFC proceeds to the following scheme:



SCHEME I

where under the ratio $x:y=1:0.95$ $m=4$ (I); $x:y=1:1$, $m=12$ (II).

As it is seen the ratio of reacting products has a great influence on the depth of HFC. In the case of equimolecular ratio the depth of HFC achieves its maximum values. The obtained oligomers are transparent glass type systems soluble in organic solvents with $\eta_{spec}=0.04$–0.05. Some physical–chemical properties of oligomers presented in the Table I.

In the IR spectra of oligomers I, II in the region 1000–1100^{-1} cm one can observe the absorption bands for asymmetric valence oscillation of the Si—O—Si bonds at 1075 cm^{-1} and 1020 cm^{-1}

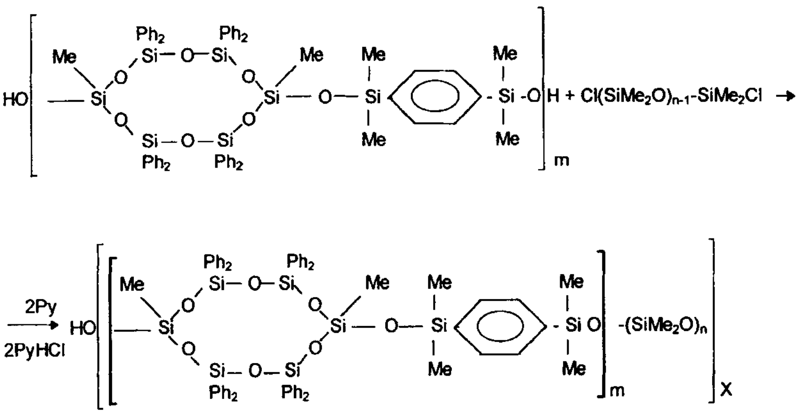
TABLE I Some physical–chemical properties and yields of oligomeric α,ω-dihydroxysilarylencyclohexasiloxanes

Oligomer	*Yield, %*	T_{soft}, °C	η_{sp}	*OH, %* *Found*	*Calcul.*	d_1, Å	M^* *Found*	*Calcul.*
I	80	61–65	0.04	0.76	0.74	10.04	4600	4554
II	86	67–71	0.05	0.21	0.25	10.08	14200	13626

characteristic for Si—O—Si bonds in cyclohexasiloxane ring and in the linear siloxane link accordingly, which testify that during HFC the reaction of polymerization of cyclic fragments does not take place.

Thermogravimetric investigations of oligomers show that for oligomer II 5% mass losses observe at 420°C temperature. The main destruction process proceeds in the range 500–650°C and above 700°C the mass losses do not occur. At 1000°C residual mass consists 42%.

By X-ray analysis it was established that the oligomers are amorphous systems, where the first diffraction maximum d_1 interchain distance changes in the region 10.04–10.08 Å (Fig. 1). By the HFC of α,ω-dihydroxysilarylencyclohexasiloxane oligomers with α,ω-dichlordimethylsiloxanes, with the ratio of initial components 1:1, in 60–70% anhydrous toluene solution, in the presence of pyridin it was synthesized $(AB)_mC_n$ silarylencyclohexasiloxane-dimethylsiloxane block-copolymers, by following scheme:



SCHEME II

where $m=4$, $n=2$ (II), 4 (IV), 12 (V), 32 (VI), 66 (VII).

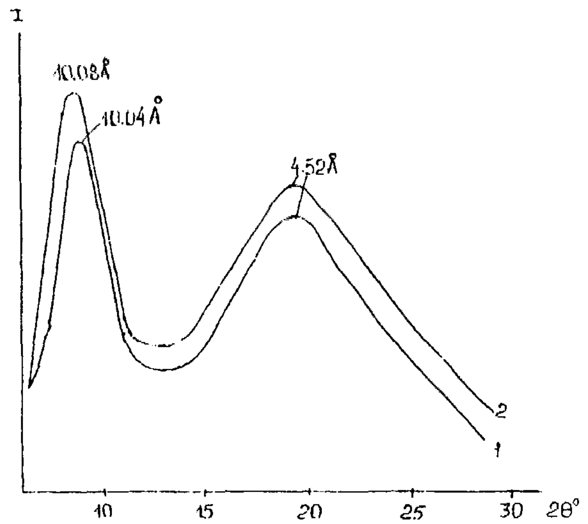


FIGURE 1 Diffractograms of α,ω-dihidroxysilarylencyclohexasiloxane oligomers, where curve 1 is for oligomer I, curve 2 is for oligomer II.

The obtained block-copolymers are light-yellow viscous or solid products (depending of the value *n*) well soluble in the organic solvents, with $\eta_{spec} = 0.10 - 0.29$.

It was carried out the fractionation of copolymer V by partially reprecipitation from toluene solution by methanole. It was obtained four fractions ($V^1 - V^4$) elementary analyses of these fractions showed that they distinguished a little from each other. All these showed that during HFC the reaction of homofunctional condensation improbable and block-copolymers with regular arrangement of silarylencyclohexasilixane blocks in macromolecular chain are obtained.

For block-copolymer VI it was determined characteristic viscosity $[\eta] = 0.16$ dl/g, coefficient of diffusion $D = 10.9 \times 10^{-7}$ cm^2/sec, coefficient of sedimentation $S = 4{,}1$, specific volume $\nu = 0.83$ cm^3/g, incriment of refraction $dn/dc \approx 0.07$ cm^3/g and molecular masses $M_{SD} = 49760$.

It was carried out the thermogravimetric investigations of synthesized block-copolymers in isothermic conditions at 300°C, as it is shown from Figure 2 block-copolymers with little values of the length

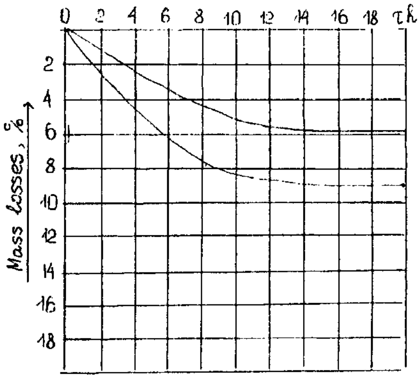


FIGURE 2 Dependence of mass losses on the time, where curve I corresponds to block-copolymer III, curve 2 corresponds to block-copolymer V. (At temperature 300°C, in isothermic conditions).

of dimethylsiloxane links *n*, are characterized with higher thermal-oxidative stability.

During 18 hours for block-copolymer III mass losses not exceed 6%. With an increase of the length of dimethylsiloxane link mass losses for block-copolymer V consists 9.5%. As it is shown from thermogravimetric investigation Figure 3, 5% mass losses can be

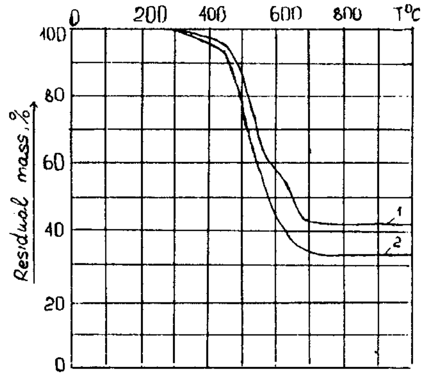


FIGURE 3 The thermogravimetric curves of block-copolymers, where curve 1 corresponds to block-copolymer III, curve 2 – corresponds to block-copolymer VI (in the air, temperature rise ratio 5 deg/min).

observed in the temperature region, 400 – 420°C. The main destruction process proceeds over the range 480 – 680°C and above 700°C curves of mass losses do not occur. Residual masses for copolymer III is 42% and for copolymer VI is 32%.

For synthesized block-copolymers it was carried out the roentgenographic investigations. As it is shown from the Figure 4 in the case of small values of the length of dimethylsiloxane links $n = 2 - 12$, the copolymers are one phase systems. On the diffractograms one can observe two maximums $2\vartheta^\circ = 8.8^\circ$ and $2\vartheta^\circ = 21.5^\circ$, the main maximum $2\vartheta^\circ = 8.8^\circ$ corresponds to the maximum value of inter-chain distance $d_1 = 10.02$ Å and $2\vartheta^\circ = 21.5^\circ$ corresponds to $d_2 = 4.52$ Å, which has more complicated nature and corresponds both intra and interchain atomic interactions [8].

With an increase of the value n block-copolymer V ($n = 12$) interchain distance value d_1 decreases and consists of $d_1 = 9.75$ Å. In

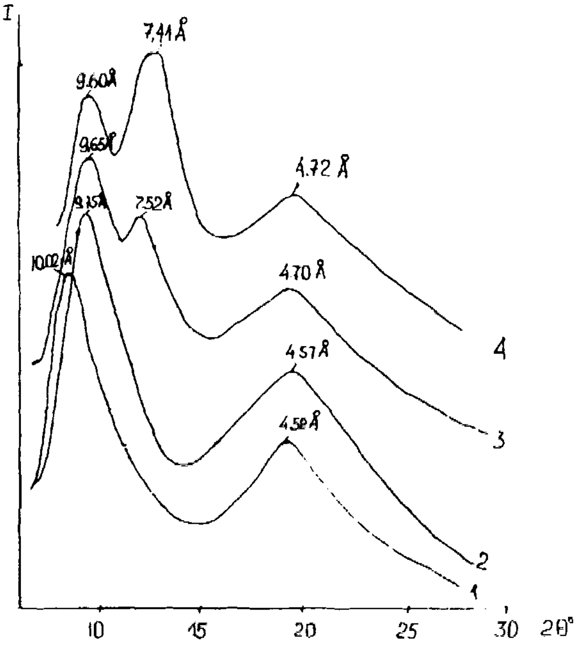


FIGURE 4 Diffractograms of block-copolymers, where curve 1 corresponds to block-copolymer III, 2 – corresponds to block-copolymer V, curve 3 corresponds to block-copolymer VI and curve 4 corresponds to block-copolymer VII.

case of higher values and the length of dimethylsiloxane links $n=32$ and $n=66$ (block-copolymers VI and VII) on the diffractograms appear the third diffraction maximum in the range $d_1=7.41-7.52$ Å, which corresponds to the interchain distance in the linear polydimethylsiloxane. The appearance of the third diffraction maximum in

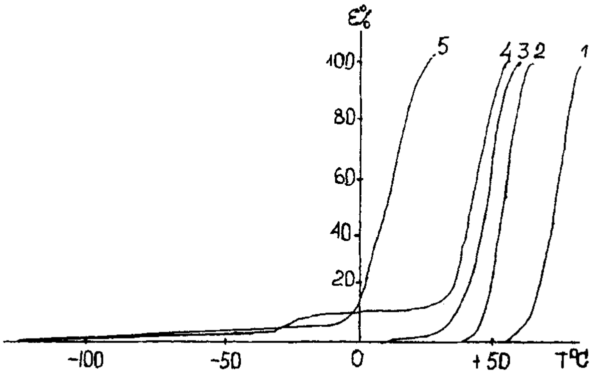


FIGURE 5 Thermomechanical curves of block-copolymers, where curve 1 corresponds to block-copolymer III, 2-IV, 3-V, 4-VI and 5-VII.

TABLE II Elementary analysis, some physical–chemical properties and yields of block-copolymers

Oligomer	*Yield, %*	η_{sp}	T_{vit}, °C	d_1, Å	*Elementary composition*		
					C	*H*	*Si*
III	91	0.13	56	10.02	64.85 65.51	5.30 5.55	20.01 20.32
IV	94	0.18	40	–	61.20 61.59	5.21 5.63	20.30 20.86
V	95	0.22	5	9.75	57.94 58.40	5.47 5.90	22.35 22.71
V′	25	0.25	–	9.65	57.80 58.40	5.61 5.90	22.41 22.71
V″	30	0.20	–	9.65	57.90 58.40	5.68 5.90	22.57 22.71
V‴	40	0.17	–	9.65	58.12 58.40	5.72 5.90	22.60 22.71
VI	95	0.27	−123	−7.52	52.30	6.21	25.60
VII	96	0.29	−123	−7.41	47.11	6.62	28.94

'In toluene at 25°C.

"In the denominator there are calculated values, in numerator experimental values.

such values of the length of dimethylsiloxane links (n) shows that we deal with two phase systems. Therefore, during formation of two phase systems when n has the definite values the segregation processes take place separately for rigid silarylencyclohexasiloxane fragments as well as for dimethylsiloxane fragments, which result in the formation of domains separately for rigid and flexible blocks and which are divided in the form of separate phases (as independent units) where each of phases are realized as independent packing.

The thermomechanical investigations of block-copolymers have been carried out. As it is ahown from Figure 5 during the little values of lengths of dimethylsiloxane links $n=12$ block-copolymers are characterized by plus vitrification temperatures. With an increase of the length of dimethylsiloxane links ($n>32$) the copolymers are characterized by the same values of vitrification temperatures as the linear PDMS.

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