# Poly(1,3-disila-1,3-diphenyl-2-oxaindane)-diphenylsiloxane-poly(dimethylsiloxane) Block Copolymers

**O. Mukbaniani, M. Matsaberidze, V. Achelashvili, N. Mukbaniani, A. Samsonia**

*Iv. Javakhishvili Tbilisi State University, I. Chavchavadze Avenue, 1, Tbilisi 0128, Republic of Georgia*

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**ABSTRACT:** The heterofunctional condensation of 1,3-dichloro-1,3-disila-1,3-diphenyl-2-oxaindane with dihydroxydiphenylsilane at various ratios of initial compounds in the presence of amines was carried out, and $\alpha,\omega$-dihydroxy(1,3-disila-1,3-diphenyl-2-oxaindane)-diphenylsiloxane oligomers with various degrees of condensation were obtained. Corresponding block copolymers were obtained by heterofunctional polycondensation of synthesized $\alpha,\omega$-dihydroxy(1,3-disila-1,3-diphenyl-2-oxaindane)-diphenylsiloxane oligomers with $\alpha,\omega$-dichlorodimethylsiloxanes in the presence of amines. Thermogravimetry, gel permeation chromatography, differential scanning calorimetry, and wide-angle X-ray analysis were carried out on the synthesized block coplymers. Differential scanning calorimetry and wide-angle X-ray studies of these copolymers showed that their properties were determined by the ratio of the lengths of the flexible linear poly(dimethylsiloxane) and rigid poly(1,3-disila-1,3-diphenyl-2-oxaindane)-diphenylsiloxane fragments in the main macromolecular chain. Two-phase systems were obtained with specific flexible and rigid fragment length values in synthesized block copolymers. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 3462–3467, 2006

**Key words:** 1,3-dichloro-1,3-disila-1,3-diphenyl-2-oxaindane; heterofunctional condensation

## INTRODUCTION

From the literature it is known that inserting more rigid phenyl fragments in the main poly(dimethylsiloxane) (PDMS) backbone hinders the cyclic depolymerizations of the polymeric chain[1] and increases the thermal– oxidative stability of copolymers. This may be explained by the presence of phenyl groups with high resistance to oxidation and their inhibiting effect on the oxidation of methyl groups.[2]

Organosilicon block copolymers (BCs) have recently received widespread attention.[3] There is information about siliconorganic BCs with a cyclolinear structure of the macromolecules. From $A_mB_n$ type cyclolinear siliconorganic BCs there are known poly-1,3-disila-1,3-diphenyl-2-oxaindane fragments in the main DMS chain,[4] ladder polyphenyl-silsesquioxanes with single- and double-stranded DMS fragments in the main chain,[5–8] polycyclotetrasiloxane–DMS BCs,[9] and disilaoxaindane–DMS BCs.[10] From $(AB)_mC_n$ type BCs there are known silarylenecyclotetra(hexa)siloxane–DMS BCs.[11,12] These publications demonstrated that phase incompatibility and formation of two-phase systems in BCs depended on the lengths of the rigid and flexible fragments. The lengths for DMS blocks from which flexible block properties start to appear must be higher than 20, whereas polycyclic (ladder) blocks even with $m \geq 3$ exhibit properties characteristic for rigid block systems.[13]

## EXPERIMENTAL

The organic solvents were purified by drying and distillation. The initial 1,3-dichloro-1,3-disila-1,3-diphenyl-2-oxaindane was procured by a well-known method.[14] The purity of the initial compounds was verified on a gas–liquid chromatography apparatus (Russian model LKhM-8MD) with a phase SKTF-100 (10%) on an NAW chromosorb with helium as the carrier gas and a 2-m column. FTIR spectra were obtained on a Nicolet Nexus 470 machine with an MCTB detector.

Gel permeation chromatography (GPC) was carried out with a Waters model 6000A chromatograph with an R 401 differential refractometer detector. The column set comprised $10^3$ and $10^4$ Å Ultrastyragel columns. Sample concentrations were approximately 3 wt % in toluene, and a typical injection volume for the siloxane was 5 $\mu$L. Standardization of the GPC was accomplished by the use of styrene or PDMS standards with known molecular weight.

Differential scanning calorimetry (DSC) analyses were carried out on a PerkinElmer DSC-7 with a cooling accessory for determination of the thermal transitions in the polymers. A temperature increase or

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*Correspondence to:* O. Mukbaniani (mukbaniani@ictsu.tsu.edu.ge).

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TABLE I
Physical–Chemical Properties of $\alpha$, $\omega$-Dihydroxy(1,3-disila-1,3-diphenyl-2-oxaindane)–diphenylsiloxane Oligomers

| No. | Yield (%) | $m$ | $\eta_{sp}$ | $d_1$ (Å) | $T_{soft}$ (C) | OH[a] (%) | $\bar{M}$[b] |
|---|---|---|---|---|---|---|---|
| I | 88 | 6 | 0.07 | 10.41 | 83–88 | 1.02 | 2990 |
| | | | | | | 1.09 | 3096 |
| II | 85 | 9 | 0.10 | 10.42 | 91–96 | 0.69 | 4490 |
| | | | | | | 0.72 | 4644 |

[a] The specific viscosity in 1% solution at 25°C. The calculated values are in the denominator, and the experimental values are in the numerator.

[b] The molecular weights were determined by ebulliometric methods and by OH end group analysis.

scanning rate decrease of ~10°C/min was used. The glass-transition temperatures ($T_g$) were read from endothermic DSC traces, which were approximated to be midpoints between the extrapolated tangents to the baselines above and below the glass-transition region.

Thermogravimetric investigations were carried out on a Paulic–Pauluc–Erday derivatograph (model MOM-102). The test conditions were a temperature rise rate of 5 deg/min in an open area.

Wide-angle X-ray analyses were carried out on a Dron-2 instrument (Russian model) using A-Cu K$\alpha$ radiation. The values were measured without a filter, and the angular velocity of the motor was ~2°/min.

### Heterofunctional condensation (HFC) of 1,3-dichloro-1,3-disila-1,3-diphenyl-2-oxaindane with dihydroxydiphenylsilane (1 : 0.95 ratio)

The polycondensation reaction was carried out in a three-necked flask equipped with a reflux condenser, dropping funnel, and mechanical stirrer. A solution of 1.6157 g (7.4803 mmol) of dihydroxydiphenylsilane in 1.2456 g (7.8741 mmol) of pyridine was added to a solution of 2.9292 g (7.8741 mmol) of 1,3-dichloro-1,3-disila-1,3-diphenyl-2-oxaindane in 3 mL of anhydrous toluene at room temperature. The reaction mixture was stirred and heated to the boiling temperature of toluene for 5 h. Subsequently, 6 mL of toluene was added and the filtered reaction mixture was washed to remove traces of pyridine hydrochloric acid. It was then dried above anhydrous $Na_2SO_4$ and reprecipitated from methanol, and 3.4 g (88%) of oligomer **I** was obtained. Oligomer **II** was produced with a 1:0.98 ratio of initial compounds via the same method. Some of the physical–chemical properties of the oligomers are presented in Table I.

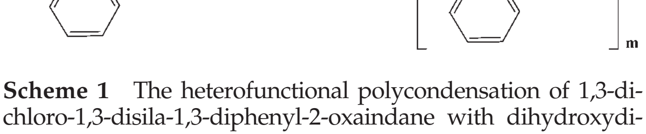
### HFC of dihydroxy(1,3-disila-1,3-diphenyl-2-oxaindane)-diphenylsiloxane oligomer I with 1,3-dichlorotetramethyldisiloxane

The polycondensation reaction was carried out in a three-necked flask equipped with a reflux condenser, dropping funnel, and mechanical stirrer. The solution of 11.2880 g (3.646 mol) of product **I** in 0.0577 g (7.292 mmol) of pyridine and 12 mL of anhydrous toluene was added to the solution of 0.7401 g (3.646 mol) of 1,3-dichlorotetramethyl disiloxane in 0.5 mL of anhydrous toluene at room temperature. The reaction mixture was stirred and heated to the boiling temperature of toluene for 5 h, and then 6 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 precipitated from methanol and copolymer **VII** was obtained. The syntheses of the other copolymers were carried out with the same method.

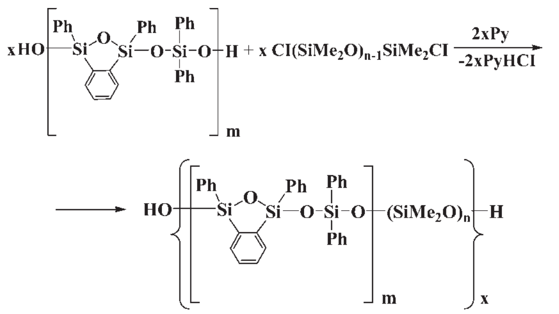
## RESULTS AND DISCUSSION

The heterofunctional polycondensation reaction of 1,3-dichloro-1,3-disila-1,3-diphenyl-2-oxaindane with dihydroxydiphenylsilane, which had 1 : 0.95 and 1 : 0.98 ratios of initial compounds in the presence of pyridine as an acceptor of hydrogen chloride in a 50–60% anhydrous solution of toluene, was investigated to synthesize disilaoxaindane fragments containing rigid oligomers. The reaction was carried out at room temperature. When the reaction was completed, the reaction mixture was heated to the boiling point of the solvent. Then, the synthesized oligomers were partially reprecipitated from the toluene solution by methyl alcohol. The HFC reaction proceeds according to Scheme 1 in which $m \approx 6$ (**I**) and 9 (**II**).

The synthesized oligomers are white solids that are soluble in ordinary aromatic solvents, with a specific viscosity ($\eta_{sp}$) of ≈0.07–0.10. Some of the physical–



**Scheme 1** The heterofunctional polycondensation of 1,3-dichloro-1,3-disila-1,3-diphenyl-2-oxaindane with dihydroxydiphenylsilane.



**Scheme 2** The heterofunctional polycondensation reaction of α,ω-dihydroxy(1,3-disila-1,3-diphenyl-2-oxaindane)-diphenylsiloxane (**I**, **II**) with α,ω-dichlorodimethylsiloxanes.

chemical properties and the yield of oligomers are presented in Table I.

In the FTIR spectra of the oligomers one can see the absorption bands in the 540 and 940, 1020 cm$^{-1}$ regions, which are characteristic of $\gamma_s$ and $\gamma_{as}$ $\equiv$Si—O—Si$\equiv$ bonds in the 1,3-disila-2-oxaindane fragment. In the 3200–3600 cm$^{-1}$ region one can see absorption bands for associated Si—OH bonds.

The synthesized α,ω-dihydroxy(1,3-disila-1,3-diphenyl-2-oxaindane)-diphenylsiloxane oligomers were used in the HFC reaction with α,ω-dichlorodimethylsiloxanes.

The HFC reactions were carried out with a 1 : 1 ratio of initial compounds in 50–60% solutions of anhydrous toluene and a temperature range of 20–25°C. At completion the reaction mixtures were heated to the boiling point of the toluene. After finishing the reaction the synthesized BCs were reprecipitated from the toluene solution by methyl alcohol. The reaction proceeds according to Scheme 2, in which $m \approx 6$ and $n = 2$ (**III**), 12 (**IV**), 21 (**V**), and 39 (**VI**); and $m \approx 9$ and $n = 2$ (**VII**), 12 (**VIII**), 21 (**IX**), and 39 (**X**).

Depending on the length of the linear flexible (PDMS) chain, the synthesized BCs were white solid or liquid systems that were well soluble in ordinary aromatic organic solvents, with $\eta_{sp} \approx 0.11–0.37$. Table II presents some of the results of the elementary analysis of the physical–chemical properties and the yields of BCs.

The structure and composition of the synthesized BCs were determined by means of elementary analysis and FTIR spectral data. In the spectra of the BCs one can observe the absorption bands in the regions of 540 and 940, 1020 cm$^{-1}$, which are characteristic of $\gamma_s$ and $\gamma_{as}$ $\equiv$Si—O—Si$\equiv$ bonds in the 1,3-disila-2-oxaindane fragment and linear DMS chain. One can also see the absorption bands for $\equiv$Si—Me and $\equiv$Si—Ph bonds at 1275 and 1435 cm$^{-1}$, respectively. BC **V** was fractionated in five fractions ($V^1–V^5$). As seen from Table II, the elementary analysis of the fractions ($V^1–V^5$) showed slight differences among them. This proved that secondary processes do not take place during HFC.

A GPC analysis of BC **V** was carried out. As seen from Figure 1, the copolymer has a monomodal molecular weight distribution with $M_{\omega;} \approx 5.59 \times 10^4$, $M_n \approx 3.38 \times 10^4$, and $M_z \approx 9.04 \times 10^4$. The polydispersity of BC **V** is ≈1.65.

Wide-angle X-ray investigations were carried out for the synthesized BCs. Figures 2 and 3 show that, with the change of the length of the flexible linear

**TABLE II**
**Physical–Chemical Properties Yields and Elementary Analysis of Poly(1,3-disila-1,3-diphenyl-2-oxaindane)-diphenylsiloxane–dimethylsiloxane BC**

| No. | Yield (%) | [η] (dL/g) in toluene at 25°C | $d_1$ (Å) | $T_g$ °C <br> $T_{cryst}$ °C | $T_{melt}$ (°C) <br> $T_{soft}$ (°C) | 10% Mass losses | Residual mass (%) | Elementary composition (%)[a] C | H | Si |
|---|---|---|---|---|---|---|---|---|---|---|
| **III** | 87 | 0.11 | 10.40 | — | +94 | 430 | 38 | 67.87 | 4.44 | 16.77 |
| | | | | | | | | 68.06 | 4.81 | 17.26 |
| **IV** | 92 | 0.15 | — | — | +85 | 450 | 35 | 61.00 | 5.01 | 20.93 |
| | | | | | | | | 61.44 | 5.42 | 21.08 |
| **V** | 94 | 0.25 | 10.10 | −121 | −42.5 | — | — | 56.78 | 5.23 | 23.11 |
| | | | 7.53 | −87.5 | +64.5 | | | 57.29 | 5.81 | 23.48 |
| **VI** | 95 | 0.35 | 9.07 | −123 | −40.0 | 400 | 9 | 51.60 | 6.10 | 26.31 |
| | | | 7.70 | −89 | +62.3 | | | 51.75 | 6.32 | 26.68 |
| **VII** | 88 | 0.13 | 10.65 | — | +94 | 470 | 41 | 68.32 | 4.21 | 16.65 |
| | | | | | | | | 68.61 | 4.75 | 16.94 |
| **VIII** | 93 | 0.17 | 10.45 | — | +75 | — | — | 63.34 | 4.97 | 19.20 |
| | | | | | | | | 63.77 | 5.21 | 19.74 |
| **IX** | 94 | 0.22 | 10.10 | −123 | −42.5 | 450 | 35 | 59.67 | 5.31 | 21.30 |
| | | | 7.65 | −90 | +62.5 | | | 60.41 | 5.51 | 21.68 |
| **X** | 96 | 0.37 | 9.56 | −120.5 | −42.5 | 420 | 18 | 55.11 | 5.60 | 24.11 |
| | | | 7.87 | −90.3 | +62.5 | | | 55.46 | 5.97 | 24.54 |

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

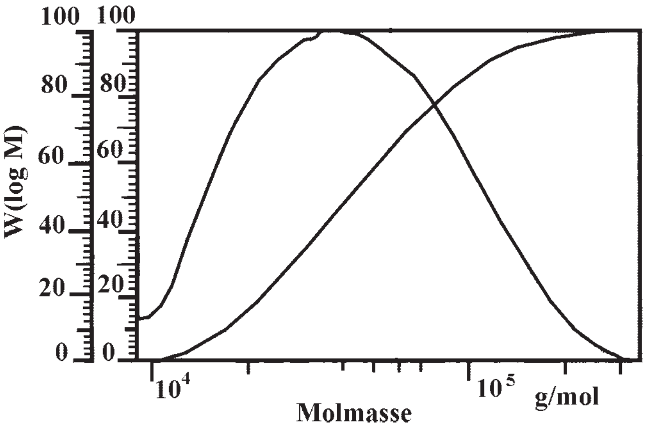


**Figure 1** The gel permeation chromatography curve of BC **V**.

PDMS segment on the diffractograms, one can observe the phase incompatibility in amorphous BCs. At small values of DMS segments the BCs are represented as one-phase systems. The maximum value of interchain distances was achieved at a small value of the PDMS segment ($n$ = 2). The diffractograms revea; two diffraction maxima at $2\theta^0 \approx 8.25°$ and 19.50–19.75°. The interchain distance ($d_1$), which corresponds to $2\theta^0 \approx 8.25°$, is ≈10.75 Å. This value of $d_1$ is near the interchain distances of poly(1,3-disila-1,3-diphenyl-2-oxaindane)-DMS BCs, whose value is 11.05 Å.[12] The second maximum ($d_2$) corresponds to ≈4.55 Å, which characterized both intra- and interchain atomic interactions.[15]

With the increase of the length of PDMS chain ($n \geq 21$) the flexible block properties characteristic for the PDMS segment started to appear, and two-phase systems were obtained. At this time the $d_1$ value characteristic for rigid poly-(1,3-disila-1,3-diphenyl-2-oxa-indane)-diphenylsiloxane blocks decreased and changed in the range of 9.56–10.10 Å. The diffractograms revealed the third diffraction maximum at $2\theta^0$ 11.25–11.75°, which characterized the interchain distances of the flexible PDMS segments and changed ≈7.53–7.87 Å in the $d_1$ range. The appearance of the third diffraction maximum with a $d_1$ range of ≈7.53–7.87 Å showed that with such values for the length of the flexible fragments we have dealings with incompatibility of phases (BCs) structure.

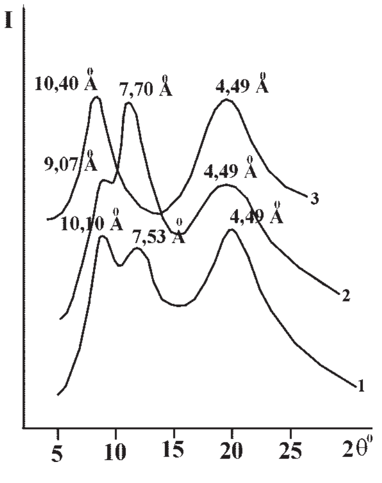


**Figure 2** The X-ray diffraction patterns of poly(1,3-disila-1,3-diphenyl-2-oxaindane)-diphenylsiloxane–dimethylsiloxane BCs: copolymers **V** (curve 1), **VI** (curve 2), and **III** (curve 3).

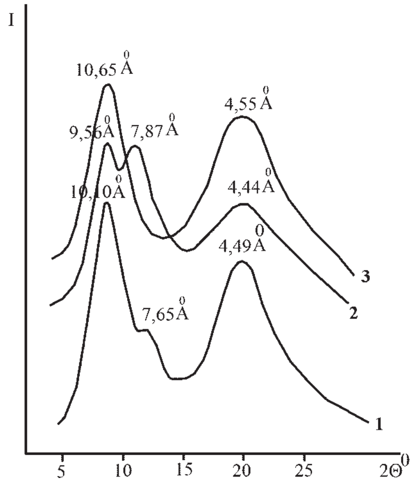


**Figure 3** The X-ray diffraction patterns of poly(1,3-disila-1,3-diphenyl-2-oxaindane)-diphenylsiloxane–dimethylsiloxane BCs: copolymers **IX** (curve 1), **X** (curve 2), and **VII** (curve 3).

Poly(1,3-disila-1,3-diphenyl-2-oxaindane)-diphenylsiloxane–DMS BCs were studied by the DSC method. At small values of the flexible PDMS chain ($n < 21$) the copolymers were represented as one-phase systems with one glass-transition temperature ($T_g$) in the range of ≈+67–+94°C, as shown in Figure 4 (curve 1). With an increase of the length of the PDMS chain ($n \geq 21$) the DSC curves show two transition temperatures at a $T_g$ of ≈−123°C, which is characteristic for a flexible linear PDMS chain, and at a melting temperature ($T_{\mathrm{melt}}$) of +60−+70°C, which is characteristic for rigid (1,3-disila-1,3-diphenyl-2-oxaindane)-diphenylsiloxane blocks (Fig. 4). Crystallization temperatures ($T_{\mathrm{cryst}}$) in the −72 to −95°C range and $T_{\mathrm{melt}}$ in the −35 to −50°C range are characteristic for flexible linear PDMS chains. This melting temperature value characteristic for linear PDMS blocks changes a small amount. Thus, in contrast to literature data,[16,17] in poly(1,3-disila-1,3-diphenyl-2-oxaindane)-diphenylsiloxane–DMS BCs, as in polysilylene-polysiloxane BCs, the crystallization process is observed from the length of the PDMS chain ($n \geq 19$).[18]

Thermogravimetric investigations of the synthesized BCs were carried out. As seen from Figure 5, the BCs are characterized by higher thermal–oxidative

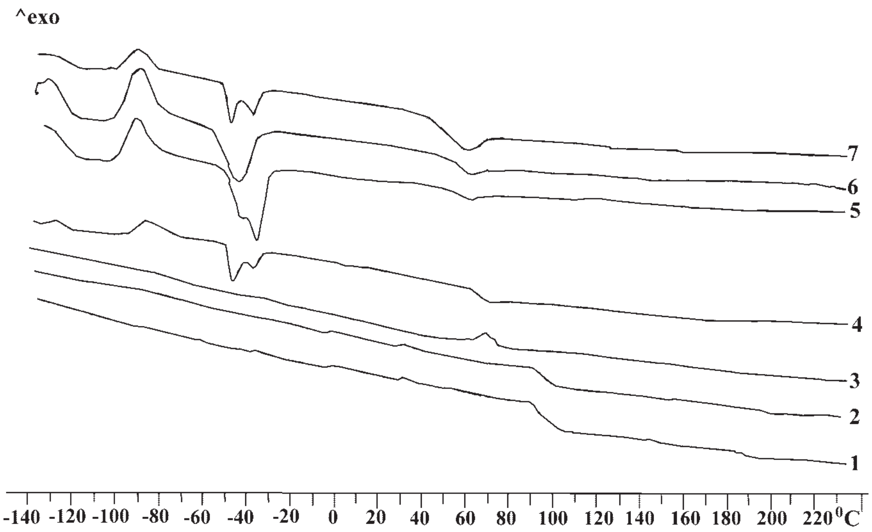


**Figure 4** DSC thermograms of poly(1,3-disila-1,3-diphenyl-2-oxaindane)-diphenylsiloxane–dimethylsiloxane BCs: copolymers **VII** (curve 1), **III** (curve 2), **VIII** (curve 3), **V** (curve 4), **VI** (curve 5), **IX** (curve 6), and **X** (curve 7).

stability than linear PDMS. Ten percent mass losses for BCs were observed at 400–460°C, and with an increase of the length of the linear PDMS chain the thermal–oxidative stability of BCs decreased. Conversely, an increase of the length of rigid 1,3-disila-1,3-diphenyl-2-oxaindane-diphenylsiloxane fragments caused the thermal–oxidative stability of BCs to rise slightly. This is explained by the presence of high thermally stable phenyl groups and their inhibiting effect on the oxidation of methyl groups.[2] This agreed with the conclusion that the insertion in the linear PDMS chain of hetereroatoms and various cyclic fragments broke the spiral structure of the copolymers and changed their physical–chemical properties.[19] These inclusions hindered the cyclic depolymerization of the PDMS chain with the release of $D_n$ $[(Me_2SiO)_n]$ type cyclosiloxanes. The main destruction process proceeded in the 450–700°C range, and above 750°C the curves of mass losses did not occur.

The heating of synthesized BCs 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 formation of gaseous products. The change of the length of linear DMS links between 1,3-disilaoxaindane cyclic fragments allowed the change of the average distances between the crosslink sites.

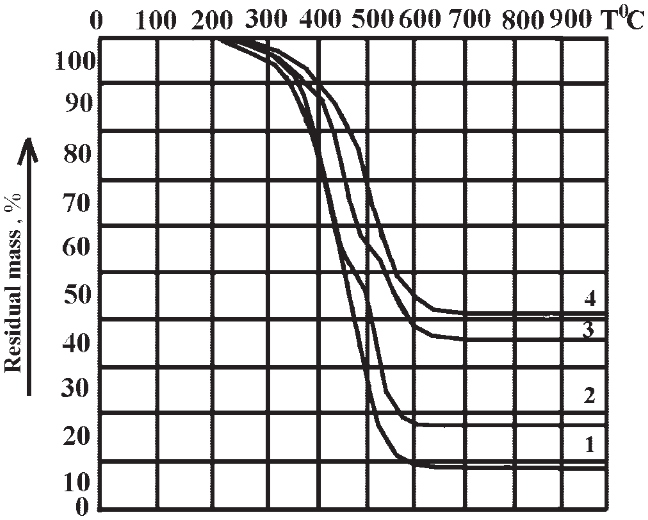


**Figure 5** Thermogravimetric curves of poly(1,3-disila-1,3-diphenyl-2-oxaindane)-diphenylsiloxan–dimethylsiloxane BCs: copolymers **VI** (curve 1), **X** (curve 2), **IX** (curve 3), and **VII** (curve 4).

## References

1. Thomas, T. H.; Kendrick, T. C. J Polym Sci Part A-2: Polym Phys 1969, 17, 537.
2. Bulkina, A. F.; Papkov, V. S.; Zhdanov, A. A.; Andrianov, K. A. Vysokomol Soedin 1978, 20A, 70.
3. Noshay, A.; McGath, J. E. Block Copolymers; Academic Press: New York; 1977.
4. Mukbaniani, O. V.; Matsaberidze, M. G.; Karchkhadze, M. G.; Khananashvili, L. M.; Achelashvili, V. A. Russ Polym News 2002, 7, 7.
5. Mukbaniani, O. V.; Achelashvili, V. A.; Karchkhadze, M. G.; Tkeshelashvili, R. Sh.; Levin, V. Yu.; Khananashvili, L. M. Int J Polym Mater 1992, 18, 129.
6. Khananashvili, L. M.; Mukbaniani, O. V. Macromol Chem Suppl 1984, 6, 77.
7. Andrianov, K. A.; Nogaideli, A. I.; Tsvankin, D. Ya.; Makarova, N. N.; Mukbaniani, O. V. Dokl Acad Nauk USSR 1976, 229, 1353.
8. Mukbaniani, O. V.; Achelashvili, V. A.; Levin, V. Yu.; Khananashvili, L. M. Vysokomol Soedin 1991, A-33, 275.
9. (a) Andrianov, K. A.; Khananashvili, L. M.; Makarova, N. N.; Mukbaniani, O. V.; Meladze, S. M.; Koiava, N. A. USSR Pat.

757,555, 1980; (b) Andrianov, K. A.; Khananashvili, L. M.; Makarova, N. N.; Mukbaniani, O. V.; Meladze, S. M.; Koiava, N. A. USSR Pat. 757,555 (SU757555); Bull Invention, 1980, p 31.

10. Mukbaniani, O. V.; Matsaberidze, M. G.; Karchkhadze, M. G.; Khananashvili, L. M.; Achelashvili, V. A. Proc Georgian Acad Sci 2000, 26, 72.
11. Mukbaniani, O. V.; Achelashvili, V. A.; Khananashvili, L. M.; Levin, V. Yu.; Komalenkova, N. G.; Chernishev, E. A. Vysokomol Soedin 1990, A-32, 480.
12. Mukbaniani, O. V.; Karchkhadze, M. G.; Matsaberidze, M. G.; Achelashvili, V. A.; Khananashvili, L. M.; Kvelashvili, N. G. Int J Polym Mater 1998, 41, 103.
13. Khananashvili, L. M.; Mukbaniani, O. V. Int J Polym Mater 1994, 27, 31.
14. Chernishev, E. A.; Komalenkova, N. G.; Klochkova, T. A.; Kuzmina, G. M.; Bochkarev, V. N. Zh Obshch Khim 1975, 45, 2299.
15. Andrianov, K. A.; Kononov, L. N.; Tsvankin, D. Ya. Vysokomol Soedin 1968, 10B, 320.
16. Andrianov, K. A.; Slonimsky, G. L.; Levin, V. Yu.; Zhdanov, A. A.; Godovsky, Yu. K. J Polym Sci Part A-1: Polym Chem 1972, 10, 1.
17. Andrianov, K. A.; Slonimsky, G. L.; Levin, V. Yu.; Zhdanov, A. A.; Godovsky, Yu. K. J Polym Sci Part A-1: Polym Chem 1972, 10, 23.
18. Mukbaniani, O.; Scherf, U.; Karchkhadze, M.; Tatrishvili, T.; Khananashvili, L. Int J Polym Mater 2001, 48, 311.
19. Mileshkevich, V. P. Kautsch Rez 1978, 6, 4.