Cyclolinear Organosilicon Copolymers with Monocyclic Fragments in the Side Chain

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ABSTRACT: The reaction of heterofunctional condensation of organodichlorosiloxycyclotri(tetra, penta) siloxanes and organodichlorosililcarbocyclotrisiloxane with dihydroxydimethylsiloxanes in the presence of pyridine was investigated. It was shown that at small lengths of the linear dimethylsiloxane link ($n \leq 4$) the reaction of heterofunctional condensation runs both intermoleculary with formation of polymers and intramoleculary with formation of bicyclo-organosiloxanes. It was established that insertion of cyclic fragments in the side chain hinders the chain transfer reactions that proceed with release of the D-type cycles during thermal depolymerization. The conformational and hydrodinamic properties of some polymethylsiloxane copolymers with cyclosiloxane fragments in the side chain have been studied. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 583–594, 1999

Key words: organosilicon polymers; heterofunctional polycondensation; cyclolinear copolymers

INTRODUCTION

Before our investigations[1,2] there was no information in literature about branched dimethylsiloxane copolymers containing diorganocyclosiloxane fragments, rather than of linear dimethylsiloxane links.[3] From literature, it is known[4] that the main difference between oligo(dimethyl)methylsiloxanes of branched structure and equal viscosity linear oligodimethylsiloxanes is the absence of a tendency to crystallize at definite branching methylsilsesquioxane links. The main reason for crystallization suppression in oligo(dimethyl)methylsiloxanes is the break in regular structure of the linear siloxane chain with insertion of methylsilsesquioxane links.

EXPERIMENTAL

Organic solvents were purified by drying and distillation. The initial organodichlorosiloxyorganocyclosiloxanes and organodichlorosililcarbosiloxanes were synthesized by well-known methods.[5] The α,ω-dihydroxydimethylsiloxanes were synthesized by hydrolysis of corresponding α,ω-dichlorodimethylsiloxanes. The IR spectra of all the samples were taken on an IR-20 spectrophotometer, and the NMR spectra on a Perkin–Elmer R-32 instrument at an operating frequency of 90 MHz in a solution of CCI_4 and dioxane, with an internal standard HMDS or tetramethylsilane (TMS). NMR spectra ^{29}Si were taken on an WP-200 SY (Bruker) instrument at an operating frequency ^{29}Si -39.77 MHz. Molecular weight distribution analysis was carried out by GPC on an XЖ instrument (USSR).

The investigation of average molecular weights was carried out on an osmometer Wescan (USA) in a toluene solution at 320 K. The fractionation

Table I   Elementary Analysis, Some Phisical–Chemical Properties and Yields of Copolymers with Carbophenylcyclosiloxane Fragments in the Side Chain

Copolymer N	Yield (%)	T_g °C	d_1, Å	η sp. 1% Solution in Toluene at 25°C	Elementary Analysis, %[a]		
					C	H	Si
XII	72	0 ± 7	10.05	0.07	56.21	5.87	23.84
					55.65	6.09	24.35
XIII	74	−20	——	0.10	50.62	7.04	25.91
					51.55	6.44	26.73
XIV	89	−65	——	0.13	46.83	7.12	29.85
					47.23	6.97	30.05
XV	94	−123	7.42	0.20	38.04	7.32	34.32
					37.63	7.74	34.76
XVI	95	−123	——	0.26	35.82	7.43	35.27
					36.16	7.74	35.69
XVII	73	+16	10.40	0.06	59.76	5.62	20.95
					60.13	5.33	20.89
XVIII	80	−2	——	0.08	57.11	5.32	22.81
					56.35	5.71	23.20
XIX	88	−40	——	0.10	51.05	5.81	27.02
					51.23	6.22	26.34
XX	92	——	7.50	0.15	40.01	6.62	32.95
					40.29	7.32	33.03
XXI	95	−123	——	0.21	37.63	6.88	34.65
					38.12	7.54	34.36

[a] Numerator: calculated values; denominator: experimental values.

of copolymers was carried out using two methods: (1) by raising the temperature; and (2) by dropping the temperature. The viscosities of copolymers was investigated in toluene solutions at the 25°C. The purity of the obtained bicycloorganosiloxanes was verified by gas–liquid chromatography ЛХM-8МД (USSR), phase SKTF-100 (10%) on the NAW chromosorb, carrier gas was He on a 2-M column. The X-ray curves were taken on a ДРОН-2 instrument (USSR). A-Cu$_\alpha$, were measured the angular velocity of the motor w = 2 deg/min without a filter. Thermomechanical data were obtained at a heating rate of V = 5 deg/min and stress σ = 0, 1 Kg/cm^2. Thermogravimetric investigations were carried out on a Paulic–Paulic–Erdey derivatograph, model MOM-102. The test conditions were: temperature rise rate V = 5 deg/min, weight = 100 mg, in the open area.

Heterofunctional Polycondensation of Phenyldichlorosiloxypentaphenylcyclotrisiloxane 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 2.0642 g (0.0029 mole) phenyldichlorosiloxypentaphenylcyclotrisiloxane in 2 mL of anhydrous toluene at room temperature the solution of 0.4833 g (0.0029 mole) 1,3-dihydroxytetra-methyldisiloxane 0.5176 g (0.0058 mole) of pyridine and 0.5 mL anhydrous toluene was added. The mixture was stirred and heated to the boiling temperature of toluene for 4 to 5 h. After that, 8 mL of toluene were added. The filtered reaction mixture was washed from the traces of pyridine hydrochloric acid, dried above anhydrous Na_2SO_4, and reprecipitated from

Table II Elementary Analysis, Some Phisical–Chemical Properties and Yields of Copolymers with Phenylcyclosiloxane Fragments in the Side Chain

Copolymer N	Yield (%)	T_g °C	d_1, Å	η sp. 1% Solution in Toluene at 25°C	Elementary Analysis, %[a]		
					C	H	Si
I	73	+18	10.05	0.08	59.98	5.84	20.34
II	78	+20 0 ± 5	——	0.11	59.85 54.92	5.24 6.12	20.95 23.27
III	85	−38	——	0.14	55.58 50.41	5.68 5.71	23.58 26.33
IV	94	−115	——	0.20	50.08 39.02	6.26 7.68	26.97 33.25
V	95	−123	7.54	0.24	39.37 37.16	7.38 7.82	33.56 33.95
VI	76	+5 ± 10	8.64	0.06	37.40 57.00	7.59 5.12	34.28 22.18
VII	77	0	——	0.08	56.46 54.81	5.35 5.25	22.46 24.67
VIII	80	−12	——	0.12	54.56 52.97	5.65 5.95	24.28 25.63
IX	85	−50	7.59	0.19	53.42 47.26	6.39 6.21	25.57 28.35
X	94	−108	——	0.28	47.63 38.75	6.42 7.31	28.37 33.86
XI	94	−123	7.31	0.37	38.22 36.41	7.46 7.39	34.23 35.51
					36.55	7.65	35.27

[a] Per Table I.

methanole. The syntheses of other copolymers were carried out with the same method.

Heterofunctional Condensation of Methyldichlorosiloxypentaphenylcyclotrisiloxane with 1,5-Dihydroxyhexamethyltrisiloxane

To a solution 22.0 g (0.03 mole) methyldichlorosiloxypentaphenylcyclotrisiloxane in 400 mL of anhydrous ether at −5––10°C temperature a solution of 8.1 g (0.03 mole) 1,5-dihydroxyhexamethyltrisiloxane in 150 mL anhydrous ether and a solution of 5.6 g (0.06 mole) of anhydrous aniline in 100 mL anhydrous ether were added. The reaction mixture was stirred and heated at reflux for 3–4 h. The residue was filtered off, the solvent was evaporated, and 23.0 g viscous residue was obtained. After distillation of 23.0 g of product in vacuo, 13.2 g (58%) of pure product XXXI was isolated T boil = 120–123°C, at $P = 2 \times 10^{-2}$ mmHg, T melt = 62–63°C. IR bands: 1275 (SiMe), 1000, 1435 (SiPh), 1020, 1080 (SiOSi), 2900–3000 (CH). Calcd for $C_{37}H_{46}Si_7O_8$, %: C 55.02; H 4.91; Si 24.31; $M = 823$. Found %: C 54.55; H 5.25; Si 24.08; $M = 814$.

Heterofunctional Condensation of Methyldichlorosiloxyheptamethylcyclotetrasiloxane with 1,7-Dihydroxyoctamethyltetrasiloxane

To a solution of 23.2 g (0.06 mole) of methyldichlorosiloxyheptamethylcyclotetrasiloxane in 400 mL of anhydrous ether at −5––10°C, a solution of 17.7 g (0.06 mole) 1,7-dihydroxyoctamethyltetrasiloxane in 150 mL anhydrous ether and a solution of 10.5 g (0.12 mole) of anhydrous aniline

Table III   Elementary Analysis, Some Phisical–Chemical Properties and Yields of Copolymers with Methylcyclosiloxane Fragments in the Side Chain

Copolymer N	Yield (%)	T_g °C	d_1, Å	η sp. 1% Solution in Toluene at 25°C	Elementary Analysis, %[a]		
					C	H	Si
XXII	82	−90	7.83	0.032	27.81	6.34	39.01
XXIII	76	−95	——	0.10	27.90	6.97	39.07
					28.11	6.94	38.51
XXIV	76	−100	——	0.06	28.57	7.14	38.88
					28.31	7.02	37.92
XXV	82	−105	8.19	0.03	28.57	7.14	38.09
					28.31	7.16	38.33
XXVI	78	−110	——	0.06	28.57	7.14	38.88
					26.12	6.42	40.44
XXVII	76	−118	——	0.08	27.27	6.60	40.87
					29.13	7.16	38.16
XXVIII	82	−83	8.76	0.05	29.44	7.36	38.65
					35.93	6.37	34.41
XXIX	75	−88	——	0.08	36.04	6.71	34.63
					34.81	6.32	34.27
XXX	81	−96	——	0.10	35.07	6.77	34.46
					35.11	6.70	34.12
					35.29	7.00	35.29

[a] Per Table I.

in 100 mL anhydrous ether were added. The reaction mixture was stirred and heated at reflux for 3–4 h. The residue was filtered off, the solvent was evaporated, and 33.2 g viscous residue was obtained. After distillation of 33.2 g of product in vacuo, 17.2 g (51%) of pure product XXXIII was isolated. T boil = 93–95°C at $P = 2 \times 10^{-2}$ mmHg, $n_D^{25} = 1.4031$, $d_4^{25} = 1.0135$. IR bands: 1275 (SiMe), 1080 (SiOSi), 2900–3000 (CH). Calcd $C_{16}H_{48}Si_9O_{10}$, %: C 29.45; H 7.36; Si 38.65; $M_{RD} = 157.7$; $M = 652$. Found %: C 29.43; H 7.00; Si 38.30; $M_{RD} = 157.5$; $M = 687$. The typical reaction of synthesis of product XXXII was carried out using the above-mentioned method.

RESULTS AND DISCUSSION

Synthesis of Cyclolinear Copolymers with Monocyclic Fragments in the Side Chain

For synthesis of the linear organosiloxane copolymers with the regular arrangement of the cyclosi-

Figure 1 ^{1}H- and ^{13}C-NMR spectra of compound XXXIII.

loxane fragments in the side chain was carried out using the reaction of heterofunctional condensation (HFC) of organodichlorosiloxyorganocyclosiloxanes with α,ω-dihydroxydimethylsiloxanes and dihydroxydimethylsilane in the presence of pyridine as an acceptor of hydrogen chloride, because it is known that use of an acceptor leads to an increase of depth of HFC.[6] The reaction was carried out at room temperature. At the completing stage, the reaction mixture was heated to the boiling point of solvent. At small lengths of the linear dimethylsiloxane link, the copolymer yield was low. When the heterofunctional polycondensation of organodichlorosiloxyorganocyclosiloxanes was studied with 1,5-dihydroxyhexame-thyltrisiloxane, low-molecular

Figure 2 IR spectra of octamethylcyclotetrasiloxane (a) and copolymer XXII (b).

Figure 3 IR spectra of decamethylcyclopentasiloxane (a) and copolymer XXV (b).

products were found, after polymer reprecipitation from the mother solution, which, according to their composition and structure, corresponds to a bicyclic compound. Consequently the above-mentioned reaction of HFC proceeds to the following scheme. Where: $m = 1$, R=R'=R''=Ph, A=O: $n = 2(I)$, 4(II), 8(III), 34(IV), 51(V);

Figure 4 ^{29}Si-NMR spectra of copolymer XXII.

m = 1, R=R'=Ph, R''=Me, A=O: n = 2(VI), 3(VII), 4(VIII), 8(IX), 34(X), 51(XI); m = 1, R=Ph, R'=R''=Me, A=C$_2$H$_4$: n = 2(XII), 4(XIII), 8(XIV), 34(XV), 51(XVI); m = 2, R=R'=Ph, R''=Me, A=O: n = 2(XVII), 4(XVIII), 8(XIX), 34(XX), 51(XXI); m = 2, R=R'=R''=Me, A=O: n = 1(XXII), 2(XXIII), 3(XXIV); m = 3, R=R'=R''=Me, A=O: n = 1(XXV), 2(XXVI),

Figure 5 ^{29}Si-NMR spectra of copolymer XXV.

Figure 6 GPC of copolymer XXII.

3(XXVII); m = 3, R=R'=Me, R''=Ph, A=O: n = 1(XXVIII), 2(XXIX), 3(XXX).

The copolymers depending on silicon substituents are transparent or slightly opalescent substances, soluble in ordinary organic solvents with η_{spec} = 0.04–0.4. The yield of obtained copolymers is 72–95%. Some physical–chemical properties, elementary analysis, and yield of copolymers are listed in Tables I–III. As is shown from the data of Tables I–III at small lengths of the dimethylsiloxane links (n = 2–4) the yield of synthesised copolymers is slightly lower, which may be explained by the fact that in addition to the reaction of intermolecular condensation, there partially takes place intramolecular cyclization with formation of bicyclic compounds about $\sim$ 8%. After reprecipitation of synthesized copolymers (VII, XXIV, and XXVII) from the mother solution of toluene after removal of solvent, products were obtained with the Scheme 2. For this, products were determined molecular masses, IR, and NMR spectra. On the basis of these results, the bicyclic

Figure 7 GPC of copolymer XXV.

Table IV Viscosity and Molecular Weight Characteristics of Copolymer XXII

Fraction N	$[\eta]$ dl/g in Toluene 25°C	$\bar{M}_n$ in Acetone	$\lg[\eta]$	Weight of Fraction P_i, g	Mass Lot of Fraction W_i	Correct Summarized Mass Lot of Fraction Σ_{wi}
1	0.020	3080	−1.6989	0.6127	0.1127	0.0564
2	0.0204	1916	−1.6989	2.7165	0.4994	0.5558
3	0.027	4207	−1.5686	0.3047	0.0560	0.6118
4	0.021	3450	−1.6778	0.7522	0.1383	0.7501
5	0.031	5227	−1.5086	0.2956	0.0543	0.8044
6	0.026	5073	−1.5850	0.2248	0.0413	0.8457
7	0.035	6634	−1.4559	0.2398	0.0441	0.8898
8	0.0275	——	−1.5607	0.1565	0.0288	0.9186
9	0.0358	9375	−1.4461	0.1365	0.0251	0.9437
10	0.021	2116	−1.6778	5.4396	1.000	——

structure of this products was proved. Such products of bicyclic structures were obtained directly by the HFC of organodichlorosiloxyorganocyclosiloxanes with 1,5-dihydroxyhexamethyltrisiloxane with a 1 : 1 ratio of the initial components in the presence of aniline, 5% solution of ether at −5 to −10°C according to the following scheme:

$$[R_2SiO]_m\text{-Si-O-SiCl}_2 + HO(SiMe_2O)_n\text{-H} \xrightarrow[-2PyHCl]{2Py} [R_2SiO]_m\text{-SiOSi-}[OSiMe_2]_m$$

Where:

R=R'=Ph, R''=Me, $m = 2$, $n = 3$ (XXXI);
R=R'=R''=Me, $n = m = 3$ (XXXII);
R=R'=R''=Me, $n = 4$, $m = 3$ (XXXIII).

The composition and structure of compounds XXXI–XXXIII were determined by means of elementary analyses, by finding molecular masses, and IR and NMR spectra data.

Spectral Investigation

In the IR spectra of all the synthesized compounds XXXI–XXXIII, we can see the absorption band for asymmetric valence oscillation of the Si—O—Si bonds in the region 1020, 1075, and 1080 cm^{-1}, respectively. We can also see the absorption bands of Si—Ph, Si—Me bonds at 1000, 1445 cm^{-1} and 1275 cm^{-1}, accordingly. In the ^{1}H-NMR spectra of the compound XXXI, we can observe the singlet signal for methyl group (3H), with chemical shift $\delta = 0.11$ ppm, and two pairs of enantiotopic methyl group distinguished in space disposition with reference to methylcyclotetrasiloxane fragments Me^{4a}, Me^{8a}, and Me^{4b}, Me^{4b} with chemical shifts $\delta = 0.12$ and $\delta = 0.13$ ppm and methyl groups Me^{6a} and Me^{6b} (this group does not exchange) at $\delta = 0.14$ ppm. Moreover, in the spectrum, a complicated multiplet is observed in the region 6.8–7.4 ppm. Figure 1 shows ^{1}H- and ^{13}C-NMR spectra of compound XXXIII. In the IR spectra of obtained copolymers in the region 1000–1100 cm^{-1}, characteristics for asymmetric

Table V Viscosity and Molecular Weight Characteristics of Copolymer XXV

Fraction N	$[\eta]$ dl/g in Toluene 25°C	$\bar{M}_n$ in Acetone 25°C	$\lg[\eta]$	$\lg \bar{M}_n$
1	0.322	9585	−1.4921	3.9815
2	0.0248	3520	−1.6055	3.5465
3	0.021	2500	1.6778	3.3979
4	0.043	6270	−1.3665	3.7978
5	0.05	——	−1.3011	——
6	0.0295	1080	——	——
Unfractionated	0.032	4157–5460	−1.4979	3.6187–3.731

valence oscillations of the Si—O—Si bonds, as well as the absorption bands at 1020 cm^{-1}, where the absorption bands of linear siloxane bonds put on the absorption bands of Si—O—Si bonds in cyclotrisiloxane ring. We also can see the absorption bands for Si—O—Si bonds in cyclotetra- and -pentasiloxane rings at 1075–1080 cm^{-1}. The transition from dimethylsiloxane links with meaning $n = 2$ to $n \approx 51$ increases the signals of asymmetric valence oscillation for Si—Me bonds, as compared with Si—Ph at 1410–1412 and 1435 cm^{-1}, respectively. The structure of some synthesized copolymers was determined by IR and ^{29}Si spectra. In the Figure 2a, we can observe the absorption bands for Si—O—Si bonds in an eight-member ring (D_4) at 1075–1080 cm^{-1} and on the Figure 3a-the absorption bands for ten-member ring at 1080 cm^{-1} (D_5). It is necessary to note that in IR spectra of copolymers XXII and XXV, additional absorption bands appear at 1020 cm^{-1} characteristic for linear polydimethylsiloxanes (PDMS); however, in PDMS, these bands are narrow, but in our case, these bands are rather wide (Figs. 2b and 3b). ^{29}Si NMR spectra of copolymer XXII (Fig. 4, in chloroform) possesses the signals in the region − 19.0 to 22.0 ppm (for D links) and −65.0 to 68.0 ppm (for silsesquioxane T links). Each mentioned range contains two division groups of signals. Weak ground signals in this range (−19.00 to 19.22 ppm and −65.0 to 68.5 ppm) attributed to cyclic fragment for the structure of copolymer. Correlation of integral intensity corresponds to the suggested structure. The main signals of ^{29}Si NMR spectra of copolymer XXV (Fig. 5) disposed in the range −21.0 to 21.6 ppm (D links) and −66.5 to 68.5 ppm (T links). Within this range, it is very difficult to distinguish the signals.

Molecular Weights, Molecular Weight Distributions, Characteristic Viscosities, and Hydrodynamic and Conformational Characteristics of Copolymers

Figure 6 shows the gel-chromatography of copolymer XXII. Because the copolymer XXII was not reprecipitated, it has a wide molecular weight distribution (MWD). For copolymer XXV, the gel-chromatographic investigation was also performed (Fig. 7). It is shown that the copolymer has a narrow MWD; consequently, the copolymer XXV was reprecipitated. For copolymer XXV, the coefficient of polydispersion has been determined, which is equal to $\varepsilon = M_w/M_n = 1.23$. The fractionation of copolymers XXII and XXV was car-

Figure 8 Integral curves of distribution according to MW and [η] for copolymer XXV.

ried out, and the results are shown in the Tables IV and V.

On the basis of data of fractionation and determination $\bar{M}_n$ and intrinsic viscosity [η], the integral curves of distribution according to MW and [η] for copolymer XXV were obtained (Fig. 8). For the same copolymer XXV, the value of constant K in the Mark–Kuhn–Howinck–Sakurada equation was calculated $K = (2.38 \pm 0.01) \times 10^{-4}$, as well as the value of the parameter $\alpha = (0.5579 \pm 0.004)$. Comparison of the equilibrium rigidity parameter of the copolymer XXV with the volume cyclic substituent in a molecule of copolymer XXV results in an increase in equilibrium rigidity of

Table VI   Some Comparative Physical Properties of Copolymers

Copolymer	Polymer Unit	$M_1 = \dfrac{M_0}{\lambda_0}$	Å Segment Kuhn	Free Rotation	Factor of Brake of Rotation
1. Polyorganocyclosiloxane	(cyclic siloxane structure with Me, Si—O—Si—O, Me₂Si, SiMe₂, Me₂Si—O—SiMe₂)	100 Å	27.0		2.12
2. Polydimethylsiloxane (PDMS)	⩗Si—O⩗ with Me, Me		10.0	0.362	1.35
3. Polymethylphenilsiloxane (PMPS)	⩗Si—O⩗ with Me, Ph		22.3	0.363	1.56
4. Cis-PMPS	⩗Si—O⩗ with Me, Ph		21.2	0.365	1.97
5. Trans-PMPS	⩗Si—O⩗ with Me, Ph		22.1	0.365	2.0
6. Polydimethyldiphenylsiloxane (PDMDPS)	$\left(\text{Si—O, Me, Me}\right)_5 \left(\text{Si—O, Ph, Ph}\right)_5$		16.0	0.365	1.71

macromolecules of copolymer $A_0 = 27$ A, compared to that of polydimethylsiloxane $A_0 = 10$ A and polydimethyldiphenylsiloxa-nes $A_0 = 16$ A. Table VI presents some comparative physical data.

Thermogravimetric investigation of synthesized copolymers was performed. Figures 9–12 present thermogravimetric curves for the copolymers. Figure 9 shows that replacement of a part of methyl groups by phenyl ones, both as a silsesquioxane atom of silicon and as a cyclic fragment, results in a rise of decomposition of starting temperature up to 280–300°C, which is associated with high resistance of phenyl groups to oxidation as well as with their inhibiting effect on oxidation of methyl groups.[7] The replacement of an oxygen bridge by an ethylene group results in a slight decrease of thermal-oxidative stability of the co-polymer (Fig. 10). With an increase in the volume of cyclic fragments, that is to say, by replacement of pentaphenylcyclotrisiloxane fragment by a heptaphenylcyclotetrasiloxane, a slight decrease of a thermal-oxidative stability occurs (Fig. 11). A similar phenomenon is observed when a hepta-methylcyclotetrasiloxane fragment is replaced by a nonamethylcyclopentasiloxane. For phenyl con-

Figure 9 The thermogravimetric curves for copolymers: curve 1 corresponds to copolymer I; curve 2: VI; curve 3: X.

Figure 11 The thermogravimetric curves for copolymers: curve 1 corresponds to copolymer XVII; curve 2: XVII; curve 3: XX.

taining copolymers, 5% mass losses can be observed in the temperature region 300–350°C; and with increasing temperature, the mass losses regularly increase. The main destruction process proceeds over the range of 360–600°C. Above 700°C, the curves of mass losses do not change. For copolymers with methylcyclosiloxane fragments as a pendant groups, 5% mass losses can be observed in the temperature region 230–250°C (Fig. 12). The main destruction process proceeds over the range of 300–600°C, above 600°C, the

curves of mass losses does not occur. With an increase of the length of dimethylsiloxane chain the thermal-oxidative stability of copolymers with phenylcyclosiloxane fragments in the side chain and copolymers containing cyclotetra-, penta-, and -hexasiloxane fragments along the chain showed that they are characterized by approximately one and the same thermal-oxidative stability, because insertion of cyclic fragments in the side chain hinders the chain transfer reactions that proceed with release of the D_n-type cycles.

Figure 10 The thermogravimetric curves for copolymers: curve 1 corresponds to copolymer XII; curve 2: XIII.

Figure 12 The thermogravimetric curves for copolymers: curve 1 corresponds to copolymer XXII; curve 2: XXV.

Figure 13 Dependence of the T_g on the mole % containing of phenylcyclosiloxane fragments. Curve 1 corresponds to copolymers VI–XI; curve 2: I–V; curve 3: XVII–XXI.

Therefore, the authors claim that cyclic fragments in the side chain in the case of destruction behave like copolymers with cyclic fragments along the dimethylsiloxane chain. Thermomechanical investigation of the synthesized copolymers was performed. In Figure 13, we can observe the dependence of T_g on the mol % of phenylcyclosiloxane fragments in the side chain. As it is evident from Tables I–III that with an increase of the amount of cyclosiloxane fragments, T_g of copolymers rises. The replacement of one methyl group by a phenyl one in the silsesquioxane link leads to a rise in glass transition temperature by $\sim$ 10°C, which is in agreement with early published data.[8] Moreover, a common phenomenon for all synthesized copolymers is that an increase of the length of the linear dimethylsiloxane chain (n) decreases the glass transition temperature of the copolymers in relation to the glass transition temperature of linear polydimethylsiloxane. The insertion in the cyclic fragment diphenylsiloxy links leads to a rise of glass transition temperature of copolymers of about at $\sim$ 15°C. This is explained by the influence of the phenyl groups, whose presence in the polydimethylsiloxane chain involves a rise in the T_g.[9] With the replacement of an oxygen bridge by an ethylene group in copolymers XII–XIV, the flexibility of copolymers increases, which leads to a decrease of T_g as compared with copolymers VI–XI. As it is evident from Table III that the insertion of methylcyclotetrasiloxane fragments in the dimethylsiloxane side chain does not lead to a considerable rise of T_g; at the means of n = 1–3, the T_g changes

from -90°C to -100°C. Glass transition temperature of copolymers with methylcyclopentasiloxane fragments in the side chain decreases at the expense of increasing of flexibility of methylcyclopentasiloxane fragments. At the same length (n) of the linear dimethylsiloxane links, the difference between glass transition temperatures of copolymers with monocyclic fragments (methylcyclotetra-, -cyclopentasiloxane) in the side is about $\sim$ 10°C. With an increase of the length of the linear dimethylsiloxane link with one dimethylsiloxane unit the T_g decreases by $\sim$ 5°C (copolymers XXV–XXVII).

X-ray analysis of the synthesized copolymers showed that all copolymers are amorphous systems with two diffraction maximums. The first diffraction maximum d_1, which characterizes interchain distance, changes in the region 7.54–10.05 Å; whereas, the second one d_2 is of a more complicated nature and corresponds both to intrachain and interchain atomic distances.[10] The value of d_1 in all copolymers changes little. In the case of small values of n, the interchain distance reached its maximum value (Tables I–III). The replacement of methyl group by a phenyl one in the silsesquioxane link, the value of d_1 increases from 8.64 Å to 10.05 Å (Table I). With the replacement of heptamethylcyclotetrasiloxane fragments by nonamethylcyclopentasiloxane fragments, the value d_1 increases from 8.19 Å to 8.76 Å (Table III). Analogous increases in the value of interchain distance d_1 by the replacement of pentaphenylcyclotrisiloxane fragments by heptaphenylcyclotetrasiloxane fragments (see Table I).

CONCLUSION

We have synthesized and studied the properties of organosilicon copolymers containing the monocyclic fragments in the side chain. It was shown that insertion of cyclic fragments in the side chain. It was shown that insertion of cyclic fragments in the side chain leads to an increase of thermal-oxidative stability of copolymers, and the main destruction process proceeds about at 80–100°C higher (in the case of phenylcyclosiloxane fragments) than the destruction of unblocked linear polydimethylsiloxane (PDMS).

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