POLYMERS WITH SILICON-CARBON CHAINS FRAMED BY SILACYCLOALKANE GROUPS

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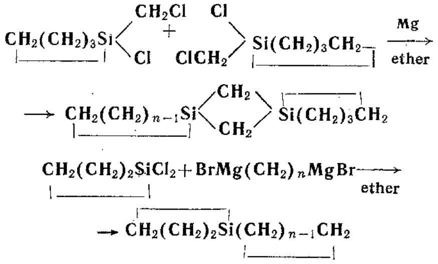
We have synthesized spiran compounds with the silicon-carbon heterocycles $CH_2(CH_2)_{n-1}Si(CH_2)_2CH_2$ (n = 4, 5) and their analogs with alkyl radicals $RR'Si(CH_2)_2CH_2$ ($R=C_2H_5$; $R'=n\text{-}C_3H_7$; C_2H_5), and also the tricyclic compound $CH_2(CH_2)_3Si\langle{}^{CH_2}_{CH_2}\rangle Si(CH_2)_3CH_2$. Their heat-induced polymerization and the properties of the resulting polymers have been investigated. The influence of the groups $-CH_2(CH_2)_{n-1}Si=$ ($n=4,5$) framing the main chain of the polymers on the stability of the chain to thermal oxidation and on its flexibility has been studied.

The present work is a continuation of preceding investigations on the synthesis of polymers with silicon-carbon main chains and on the study of their properties [1–5]. By the polymerization of strained silicon-carbon rings we have previously obtained high-molecular-weight compounds of the type of $[-R_2Si-R'-]_n$, where R' is an alkylene or arylene group and R is alkyl, aryl, or alkenyl.

We have effected the synthesis of polymers with a silacycloalkane framing of the main chain of the type $[-CH_2(CH_2)_kSi(CH_2)_m-]_n$, where m = 1 or 3 and k = = 3 or 4 and have given an evaluation of the contribution made by the silacycloalkane framing to the properties of the silicon-carbon polymer. The introduction into a polymer chain of silacycloalkane, and particularly silacyclohexane, rings is of interest for a number of reasons. Thus, it is known from the case of individual compounds of the type $R_2Si(CH_2)_4CH_2$ that the silacyclohexane group is stable to the action of strong acids and bases and possesses an increased thermal stability [6–8]. The endocyclic Si—C bond of the silacyclohexane group is extremely stable to the action of electron impact [9] and, finally, 1,1-di(n-alkyl)silacyclohexanes possess low glass points (from –50 to –60° C) [10].

The monomeric compounds used for the synthesis of these polymers were obtained by the following routes:



$$CH_2(CH_2)_3Si\langle{}^{CH_2Cl}_{Cl} + {}^{Cl}_{ClCH_2}\rangle Si(CH_2)_3CH_2 \xrightarrow[\text{ether}]{\text{Mg}} CH_2(CH_2)_{n-1}Si\langle{}^{CH_2}_{CH_2}\rangle Si(CH_2)_3CH_2$$

$$CH_2(CH_2)_2SiCl_2 + BrMg(CH_2)_nMgBr \xrightarrow[\text{ether}]{} CH_2(CH_2)_2Si(CH_2)_{n-1}CH_2$$

II ($n=4$); III ($n=5$)

The reaction was carried out as described previously [11, 12]. The properties and yields of the substances obtained are given in Table 1. Their purity was checked by means of gas-liquid chromatography and was ~96% for I and ~99.5% for II and III.

In addition, we have obtained 1,1-diethyl-1-silacyclobutane $CH_2(CH_2)_2Si(C_2H_5)_2$ (IV) and 1-ethyl-1-n-propyl-1-silacyclobutane $CH_2(CH_2)_2Si(C_2H_5)CH_2CH_2CH_3$ (V), and these have been used for the preparation of polymers the properties of which have been compared with the properties of polymers of derivatives of the spiran compounds.

Compound IV was synthesized from $CH_2(CH_2)_2SiCl_2$ and C_2H_5MgBr, and V from $CH_2(CH_2)_2Si(C_2H_5)Cl$ and C_3H_7MgBr. Their properties are also given in Table 1. Compound IV is an open-chain analog of II, and compound V an analog of III.

Thermal polymerization of the spiran compounds was carried out as a block process by the method used for silacyclobutanes [2]. Immediately before polymerization, the monomers were redistilled and were dried over lithium hydride or calcium hydride, and were then freed from dissolved gases in a vacuum of $\sim 10^{-2}$ mm. The polymer blocks were dissolved in benzene and precipitated from the solution with methanol, after which the polymer was brought to constant weight at 80–100° C (10 mm).

Polymerication of the dialkylsilacyclobutanes IV and V was carried out in purified n-decane (1 mole of monomer 4–6 moles of solvent). The temperature of polymerization, the yields of the polymers, and their characteristic viscosities, elementary compositions, and molecular weights are given in Table 2. In the block polymerization of IV and V, weakly cross-linked polymeric products are formed which swell readily in the usual organic solvents. This difference in the polymerization of the silacyclobutanes containing ethyl and propyl groups from the spiran compounds II and III and from 1,1-dimethyl-1-silacyclobutane [2] is due, in our opinion, to the reduced resistance of the $Si-C_{alkyl}$ bond to homolytic decomposition. In actual fact, according to the literature [15–17], the energy of the $Si-CH_3$ bond is 75 kcal/mole, that of the $Si-C_2H_5$ bond 62 kcal/mole, and that of the $Si-C_3H_7$-n bond 57 kcal/mole. At the same time, the endocyclic Si—C bond in the silacyclopentanes or the silacyclohexanes is even more stable than the $Si-CH_3$ bond [9]. Consequently it is likely that in bulk polymerization (exothermic reaction), the homolytic cleavage of a small number of the $Si-C_2H_5$ and $Si-C_3H_7$ bonds takes place and cross-linkages are formed at the positions of rupture.

The structure of the polymers and monomers was established by IR spectroscopy. Thus, the IR spectra

Table 1

Monomeric Silacyclanes

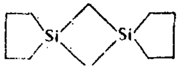
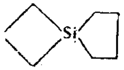
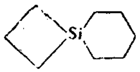
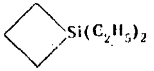
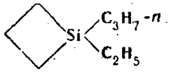
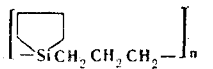
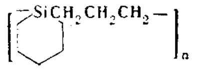
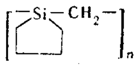
Compound	Formula	Bp, °C (pressure, mm)	n_D^{20}	d_4^{20}	MR_D		mol. wt.		Found, %			Calculated, %			Yield, %
					found	calculated	found	calculated	Si	C	H	Si	C	H	
I		123—125 (0.5)	Crystals				194	196.4	28.45	61.23	10.30	28.5	61.2	10.8	21
II		62—63 (30)	1.4850	0.8959	40.06	40.41	126	126.2	22.3	66.5	11.1	22.2	66.6	11.2	49
III		78.5 (30)	1.4875	0.8985	45.08	45.04	146	140.3	19.99	68.68	11.63	20.0	68.8	11.45	34
IV		75—76 (95)	1.4490	0.8132	42.27	42.30	128	128.3	21.68	65.59	12.5	21.9	65.6	12.5	63
V		97—98 (95)	1.4500	0.8175	46.77	47.03	141 143	142.3	20.00	67.70	12.58	19.75	67.6	12.6	80

Table 2

Polymers Synthesized

Polymer	Formula	Polymerization temp., °C	η 1* 100 ml/l	M, 10^{-6} 2*	Found, % Si	Found, % C	Found, % H	Calculated, % Si	Calculated, % C	Calculated, % H	Yield %
VI		180	1.40	1.5	23.00	65.3	11.42	22.2	66.6	11.2	60
VII		180	1.35	1.16	20.16	68.30	11.56	20.0	68.8	11.45	74
VIII		200	0.50	—	28.44	61.30	10.30	28.5	61.2	10.3	40
IX	$\left[-(C_2H_5)_2SiCH_2CH_2CH_2-\right]_n^{3*}$	180	1.25	—	23.10	65.12	12.37	21.9	65.6	12.5	70
X	$\left[-C_3H_7(C_2H_5)Si(CH_2CH_2CH_2)-\right]_n^{3*}$	180	1.30	—	20.15	67.45	12.54	19.75	67.6	12.6	71

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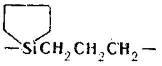
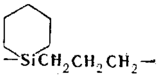
*In benzene solution at 20° C. **Determined by the light-scattering method. ***Polymerization was carried out in n-decane solution.

Table 3

Properties of the Polymeric Products

Poly mer	Structure of the link	η 100 mg/l	Structure at 20°C (from x-ray analysis)	Mp, °C 1*	Glass point according to Marey, C 2*	Thermal oxidation: temperature of initial loss of weight, °C	Thermal oxidation: temperature of the first exo effect, °C	External form
VI		1.40	Cryst.	65	−21.5	290	160—175	White, oqaque, solid
IX	$(C_2H_5)_2SiCH_2CH_2CH_2-$	1.25	Amorph.	—	—	—	3*	Colorless, transparent, rubber-like
VII		1.35	Cryst.	45	−54.5	260	140	White, semitransparent, elastic
X	$C_2H_5(C_3H_7)SiCH_2CH_2CH_2-$	1.49	Amorph.	—	—	200	3*	Colorless, transparent, rubber-like
XI	$(CH_3)_2SiCH_2CH_2CH_2-^{4*}$	2.5	Cryst.	41	−70	200	320 3* ×	White, oqaque, solid

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*Determined under the polarization microscope and from the DTA curve. **Studied on a derivatograph on the system of F. Paulik, J. Poulik, and L. Erdey, with a rate of heating of 6°C/min. ***Weakly-expressed diffuse endothermic effects are observed in the 200–300°C region. ****Described previously [2].

of the spiran compounds II and III have absorption bands at 930, 1120, and 1185 cm^{-1} which are characteristic for the 1, 1-disubstituted cyclobutane ring.

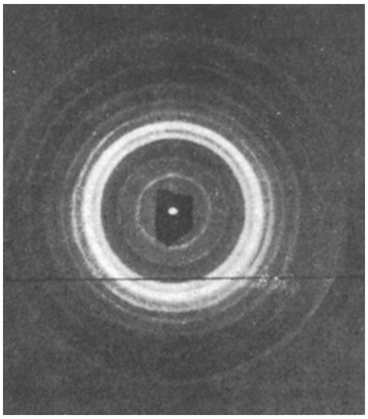
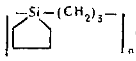


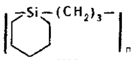
Fig. 1. X-ray diagram of poly-(trimethylenesilacyclopentane).

In the spectrum of II, absorption bands at 870, 1023, 1077, and 1150 cm^{-1} characterize the silacyclopentane ring, and in the spectrum of III, absorption bands at 913 and 982 cm^{-1} show the presence of the silacyclohexane ring. A study of the IR spectra of the products of the thermal polymerization of II and III has shown that polymerization took place with the opening of the Si—C bond of the silacyclobutane ring and the formation of linear polymeric products the links of the main chains of which are:



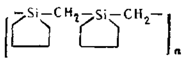
VI

and



VII

respectively. The spectra of VI and VII retain the frequencies of the silacyclopentane and silacyclohexane groups, but the absorption bonds at 930 and 1120 cm^{-1} (silacyclobutane ring) have disappeared, and a whole series of bands characterizing a trimethylene chain between Si atoms has appeared (905, 943, 990, 1025, 1080, and 1140 cm^{-1}). The tricyclic compound I behaves similarly. Its IR spectra retains the absorption bands of the silacyclopentane ring (860, 1020, 1030, 1070, and 1150 cm^{-1}) these also being observed in the spectrum of the product of the thermal polymerization of I (VIII). At the same time, the absorption of the disilacyclobutane ring in the monomer at 940 cm^{-1} changes into absorption at 1040 cm^{-1} on passing to the spectrum of the polymer. This shows the opening of the disilacyclobutane ring and the formation of a polymeric linkage of the type of



VIII

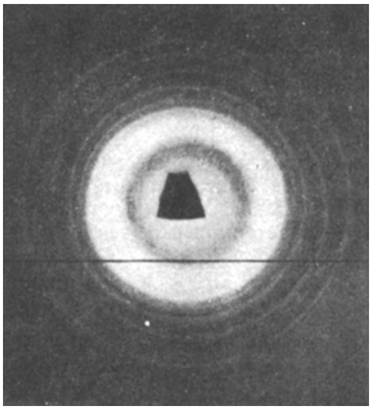


Fig. 1a. X-ray diagram of poly-(trimethylenesilacyclohexane).

The structures of the 1, 1-dialkylsilacyclobutanes IV and V synthesized and of the heterochain silicon-carbon polymers IX and X obtained from them have been established similarly. The properties of the polymers are given in Table 3.

A consideration of the information given in Table 3 may lead to the following conclusions. As suggested, the polymer VII, containing a silacyclohexane framing, possessed a comparatively low glass point (−54.5° C). Like a number of other polymeric silacyclobutanes [2], because of the high regularity of the structure of the main polymer chain, it contains a considerable volume of crystalline phase (see the X-ray diagram in Fig. 1a). The polymer with the silacyclopentane framing (VI) crystallizes even more readily than VII (Fig. 1) without annealing and melts at a higher temperature; its glass point is correspondingly lower than that of VII. The cause of this difference must apparently be sought in the greater conformational rigidity of the silacyclopentane ring as compared with the silacyclohexane ring just as is the case in their carbon analogs [13]. It is an interesting fact that the polymers with a noncyclic framing of the chain—IX and X—, which are complete structural analogs of polymers VI and VII, respectively, could not be crystallized at temperatures >0° C.

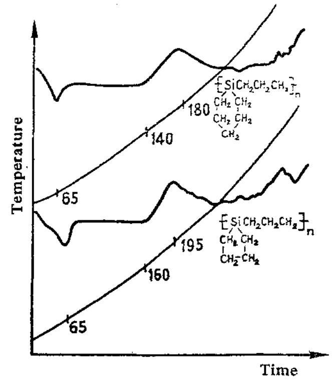
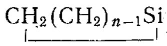
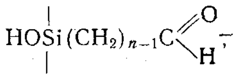


Fig. 2. Differential thermal analysis curves.

The polymer VI proved to be heat-stable. When it was heated in a vacuum of 10^{-3} mm at a rate of 2° C/ /min, loss in weight began only at 330° C and active degradation at 380° C; and 400° C the loss in weight was 7%. In the case of the polymer VII the loss in weight under conditions of thermal-oxidative degradation began at 260° C, but strong exothermic effects of oxidation appeared considerably earlier (Fig. 2). In this respect, the polymer with the silacyclohexane framing (VII) differs substantially from the polymer

XI with a dimethyl framing of the main chain, in which weak exothermic effects were observed up to 300° C [2]. At the same time, for XI the loss in weight begins at the same temperature as for VII. The open-chain structural analog (X) begins to decompose considerably earlier, although the exo effects in this are also weakly expressed. It is obvious that the framing silacyclohexane groups are responsible for this difference, increasing the number of methylene groups for each link of the polymer as compared with X and XI. This is confirmed by the fact that the exothermic effect in the polymer with the smaller number of methylene groups in the framing (VI) appears at a higher temperature (~160° C). An increase in the number of methylene groups of the framing, which are more active than methyl groups in thermal oxidation, is apparently not the only cause of the strong exo effect. Another possible cause may be the cyclic nature of the polymethylene groups framing the polymer chain, which are bound twice to the silicon atom.

In accordance with existing ideas [14], the thermal oxidation of an organic radical singly bound to silicon (Si—R) leads to the formation of an Si—OH group and to volatile oxygen-containing products which leave the reaction zone if the polymer is heated in an open system. In the oxidation of the  $\underbrace{CH_2(CH_2)_{n-1}Si}$ grouping one may expect the formation of oxygen-carbon compounds retaining a bond with the main chain of the polymer—for example of the type of  $HOSi(CH_2)_{n-1}C{\overset{O}{\underset{H}{}}}$— and therefore remaining within the polymer mass.

Aldehyde groups fixed in this way may actively promote the development of chain oxidation processes in the mass of the polymer and cause exothermic effects.

EXPERIMENTAL

1, 1-Tetramethylene-1-silacyclobutane (II). The Grignard reagent prepared from 216 g of 1, 4-dibromobutane and 72 g of magnesium turnings was added rapidly (with ice cooling) to an ethereal solution of 95 g of 1, 1-dichloro-1-silacyclobutane. The organic layer was separated off and distilled in vacuum, giving 35 g (49%) of II. The physical constants are given in Table 1.

1, 1-Pentamethylene-1-silacyclobutane (III). With cooling, 57 g of 1, 1-dichloro-1-silacyclobutane was rapidly added to the Grignard reagent obtained from 92 g of 1, 5-dibromopentane and 36 g of magnesium turnings in ether. A working-up process similar to that of the preceding experiment yielded 19 g (34%) of III, the constants of which are given in Table 1.

1, 1;3, 3-Bis(tetramethylene)-1, 3-disilacyclobutane (I). One hundred grams of magnesium turnings activated with iodine was added to 25 g of 1-chloro-1-chloromethyl-1-silacyclopentane in ether. The reaction mixture was heated for 10 hr and filtered. The yield of I was 6.1 g (21%) (see Table 1).

Polymerization conditions. The thermal polymerization of the monomers was carried out in the mass (for the spiran compounds) or in a solvent (for the alkly-substituted monosilacyclobutanes) in glass tubes with previous degassing in a vacuum of 10^{-2} mm. About 2 g of monomer was used in each batch. The polymeric products obtained were dissolved in benzene and precipitated from the solution with methanol.

REFERENCES

1. N. S. Nametkin and V. M. Vdovin, J. Polym. Sic., 1043, 1963.
2. N. S. Nametkin, V. M. Vdovin, and V. I. Zav'yalov, Izv. AN SSSR, ser. khim., 1448, 1965.
3. V. D. Oppengeim, N. S. Nametkin, V. I. Zav'yalov, K. S. Pushchevaga, and V. M. Vdovin, Izv. AN SSSR, ser. khim., 1547, 1965.
4. N. S. Nametkin, V. M. Vdovin, and V. I. Zav'yalov, Vysokomol. soed., 7, 757, 1965.
5. N. S. Nametkin, V. M. Vdovin, E. Sh. Finkel'shtein, K. S. Konobeevskii, and V. D. Oppengeim, DAN, 162, 585, 1965.
6. R. West, J. Am. Chem.Soc., 76, 6012, 1954.
7. N. A. Belikova, Candidate's thesis [in Russian], Institute of Organic Chemistry AS USSR, Moscow, 1955.
8. V. M. Vdovin, K. S. Pushchevaya, and A. D. Petrov, DAN, 141, 843, 1961.
9. N. Ya. Chernyak, R. A. Khmel'nitskii, T. V. D'yakova, V. M. Vdovin, and T. N. Arkhipova, ZhOKh, 36, 96, 1966.
10. C. Jamborski and H. Rosenberg, J. Org. Chem., 25, 246, 1960.
11. N. S. Nametkin, V. M. Vdovin, and P. L. Grinberg, DAN, 150, 799, 1963.
12. N. S. Nametkin, V. M. Vdovin, V. I. Zav'yalov, and P. L. Grinberg, Izv. AN SSSR, ser. khim., 929, 1965.
13. L. I Belen'kii and Ya. L. Gol'dfarb, Usp. khim., 29, no. 4, 470, 1960.
14. K. A. Andrianov, Polymers with Inorganic Main Chains in the Molecules [in Russian], Izd-vo AN SSSR, Moscow, p. 49, 1962.
15. S. Tannenbaum, J. Am. Chem. Soc., 76, 1027, 1954.
16. D. F. Helm and E. Mack, J. Am. Chem. Soc., 59, 60, 1937.
17. K. Waring, Trans. Farad. Soc., 36, 1142, 1940.

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