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Abstract

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Synthesis and Polymerization of Cyclotetrasiloxanes Containing Heterocyclic Radicals with a Silicon Atom

One of the methods for the synthesis of linear high-molecular-weight polyorganosiloxanes is the polymerization of organocyclosiloxanes in the presence of various catalysts. A number of examples have shown that the ability of organocyclosiloxanes to polymerize depends on the ring strain and on the nature of the organic radicals at the silicon atoms (1-5). The polymerization of mixed organocyclosiloxanes containing in the ring, along with dimethylsiloxane units, other organosiloxane units has also been described in the literature (6).

However, there are no data in the literature on the synthesis and polymerization of organocyclosiloxanes in which the silicon atom forming the siloxane chain is simultaneously part of a hydrocarbon heterocycle framing the siloxane chain. It was of interest to us to carry out the synthesis of cyclic compounds of this type and to study their polymerization.

The synthesis of a cyclotetrasiloxane of this structure was carried out by the hydrolysis reaction of 1,1-dichloro-3,4-benzo-1-silacyclohexane according to the scheme:

4 [[structural formula of 1,1-dichloro-3,4-benzo-1-silacyclohexane]]$+4H_2O \rightarrow$ [[structural formula of tetra-(3,4-

The tetra-(3,4-benzo-1-silacyclohexyl)-cyclotetrasiloxane obtained is a solid substance with a softening point of 45-50°, distilling under vacuum at 330-340°/0.5 mm without decomposition.

In studying the process of cohydrolysis of dimethyldichlorosilane with 1,1-dichloro-3,4-benzo-1-silacyclohexane, it was established that cohydrolysis proceeds with the formation of mixed cyclic compounds according to the scheme:

$n\,(CH_3)_2SiCl_2+m$ [[structural formula of 1,1-dichloro-3,4-benzo-1-silacyclohexane]]$+H_2O \rightarrow$

$$\rightarrow [(CH_3)_2SiO-]_n\,[[[\text{structural unit of 3,4-benzo-1-silacyclohexyl siloxane}]]]_m + 2(n+m)HCl,$$

where $m + n = 4$.

In this reaction, at different ratios of the reacting components, three mixed organocyclotetrasiloxanes were isolated; they were characterized by boiling point, specific gravity, refractive index, molecular weight, molecular refraction, and elemental composition. The properties of the synthesized compounds are given in Table 1.

Table 1

Compound formula	b.p., °C/mm Hg	n_D^{20}	d_4^{20}	MR calc.	MR found	Mol. wt. calc.	Mol. wt. found	C, % calc.	C, % found	H, % calc.	H, % found	Si, % calc.	Si, % found
Istructural formula: cyclotetrasiloxane containing one silicon-containing heterocyclic radical and three $(CH_3)_2Si$ units	152—154/3	1,4689	1,0571	101,30	101,30	385	383	46,82	46,61 46,58	7,33	7,38 7,42	29,20	29,29 29,30

Compound formula	b.p., °C/mm Hg	n_D^{20}	d_4^{20}	MR calc.	MR found	Mol. wt. calc.	Mol. wt. found	C, % calc.	C, % found	H, % calc.	H, % found	Si, % calc.	Si, % found
II structural formula: cyclotetrasiloxane containing two silicon-containing heterocyclic radicals and two $(CH_3)_2Si$ units	220—223/2	1,5182	1,1220	127,74	128,04	473	477	55,88	55,63 55,87	6,82	6,95 7,04	23,76	23,51 23,67

Compound formula	b.p., °C/mm Hg	n_D^{20}	d_4^{20}	MR calc.	MR found	Mol. wt. calc.	Mol. wt. found	C, % calc.	C, % found	H, % calc.	H, % found	Si, % calc.	Si, % found
III structural formula: cyclotetrasiloxane containing three silicon-containing heterocyclic radicals and one $(CH_3)_2Si$ unit	340—350/2	—	—	—	—	561	553	62,09	61,97 62,06	6,48	6,56 6,60	20,03	20,31 20,33

Fig. 1

Figure 1: Fig. 1

Compound formula	b.p., °C/mm Hg	n_D^{20}	d_4^{20}	MR calc.	MR found	Mol. wt. calc.	Mol. wt. found	C, % calc.	C, % found	H, % calc.	H, % found	Si, % calc.	Si, % found
IV structural formula cyclotetrasiloxane containing four silicon-containing heterocyclic radicals	330—340/0,5	—	—	—	—	648	615	66,61	66,99 66,94	6,21	6,80 6,82	17,31	17,35 17,48

The polymerization of the synthesized cyclic products was carried out in the presence of sulfuric acid, sp. gr. 1.84, potassium hydroxide, and tetramethylammonium hydroxide (7).

When I (designations according to Table 1) is heated with 0.2% sulfuric acid at 50, 75, and 100°, polymerization of the ring is practically not observed (Fig. 1). Possibly this phenomenon is associated with partial sulfonation of the aromatic nucleus, in which partial loss of the catalyst occurs and the remaining part of the sulfuric acid is diluted by the water that is liberated.

Fig. 1. Polymerization of organocyclosiloxanes in the presence of 0.2% H_2SO_4 at 50 (a), 75 (b), and 100° (c)

During the polymerization of I and II at 170° in the presence of 0.3 KOH, a noticeable difference can be seen in the behavior of each compound. I is readily polymerized under the indicated conditions with formation of a polymer having a reduced viscosity of 0.4, whereas for II under these conditions the polymerization process practically does not occur (Fig. 2). When the temperature is

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

raised to 190°, II begins to polymerize at an appreciable rate with formation of a polymer having a reduced viscosity of 0.2. III polymerizes very slowly at temperatures below 200°. At 220° rapid polymerization is observed, with formation of a polymer having a reduced viscosity of 0.35 (Fig. 2).

Fig. 2. Polymerization of organocyclosiloxanes in the presence of 0.3% KOH at 170° (a, c), at 190° (b), and at 22° (d)

Fig. 3. Polymerization of organocyclosiloxanes in the presence of 0.3% tetramethylammonium hydroxide. Roman numerals in Figs. 1–3 are the numbers of the compounds in Table 1

During polymerization in the presence of tetramethylammonium hydroxide, I and II at 80° polymerize very rapidly with formation of high-molecular-weight products having a reduced viscosity of 0.33 (Fig. 3). It is interesting that III practically does not polymerize in the presence of this catalyst. Possibly this is explained by the fact that the high viscosity of the initial III, even at the polymerization temperature, retards the course of the process. When the temperature is increased with simultaneous lowering of the viscosity of the system, decomposition of the catalyst occurs and its activity is lost.

In all cases, at the end point of the process the polymer contains a certain amount of insoluble phase. In polymerization with alkali, the content of insoluble phase is about 30%; in polymerization with tetramethylammonium hydroxide the content of insolubles is 1%. We assume that the formation of insoluble products is associated either with cleavage of organic radicals at elevated temperature under the action of alkaline agents, or with opening of the silicon-carbon ring, which on opening forms crosslinks between polymer molecules.

The preliminary data obtained make it possible to conclude that the activity of various catalysts with respect to the cycles studied can be characterized by the following series: $[R_4N]OH > KOH > H_2SO_4$ (inactive). The reactivity of the cycles during polymerization decreases with the accumulation of heterocyclic radicals in the molecule.

Experimental Part

Organocyclosiloxanes. For the synthesis of organocyclosiloxanes, a mixture of dimethyldichlorosilane and 1,1-dichloro-3,4-benzo-1-silacyclohexane, taken in molar ratios corresponding to the molar ratios of the units in the cycle, was hydrolyzed with water in the presence of ether. One part by weight of the organochlorosilane mixture was dissolved in an equal weight amount of ether and introduced, with stirring, into a mixture of 1 part by weight of water and 1 part by weight of ether. During hydrolysis the temperature was maintained at about 30°. After completion of the addition of the chlorosilanes, the mixture was stirred for another 1 h, the aqueous layer was separated, the organic layer was washed with water to a neutral reaction, dried over sodium sulfate, and, after removal of the solvent, fractionated under vacuum. The yield (of theoretical) of the corresponding cycles was: I 39.5%, II 22%, III 42.2%, and IV 60%.

Polymerization. The organocyclosiloxanes were polymerized in a thermostated flask, with heating in an oil bath, in a nitrogen atmosphere, with stirring. During polymerization, samples were taken at specified time intervals, and the viscosity of a 1% solution in toluene was determined for them. Sulfuric acid as catalyst was introduced directly into the organocyclosiloxane. KOH was introduced as a 20% alcoholic solution, and tetramethylammonium hydroxide as a 70% solution in octamethylcyclotetrasiloxane. The concentration of the alkaline catalysts was determined by titration for accurate dosing. The results obtained are presented in Figs. 1–3.

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Note: Figure translations are in progress. See original paper for figures.