THE COHYDROLYSIS OF γ-TRIFLUOROPROPENYLMETHYLDICHLOROSILANE WITH DIMETHYLDICHLOROSILANE AND THE POLYMERIZATION OF THE PRODUCTS OBTAINED

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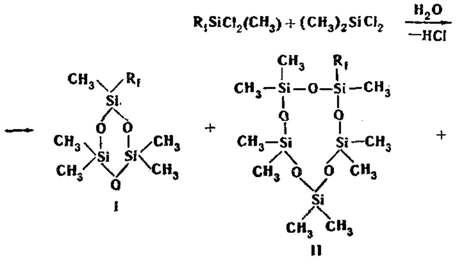
The cohydrolysis of γ-trifluoropropenylmethyldichlorosilane and dimethyldichlorosilane at 70°–75° C leads to the formation of γ-trifluoropropenylnonamethylcyclopentasiloxane, γ-trifluoropropenylpentamethylcyclotrisiloxane, and bis(γ-trifluoropropenyl)hexamethylcyclotetrasiloxane. These oligomers were polymerized in the presence of a Ziegler-Natta catalyst, forming low-molecular-weight oily polymers with M = 1000–3000.

The polymerization of unsaturated organosilicon monomers has been described many times [1,3,5–9, 11,12,15–17]. The cohydrolysis of various monomers containing unsaturated radicals on the silicon atom [2,4,10,13,14,18–20] makes it possible to obtain heterocyclic compounds with different numbers of unsaturated groups. We have studied the cohydrolysis of γ-trifluoropropenylmethyldichlorosilane with dimethyldichlorosilane and have made attempts to polymerize the cyclic oligomers obtained.

The cohydrolysis of the initial monomers took place at 70°–75° C in the following way.



$R_f = CH{=}CH{-}CF_3$;

In addition to I–III, polymeric substances were formed. Two distillations of the hydrolyzate yielded γ-trifluoropropenylpentamethylcyclotrisiloxane (I), γ-trifluoropropenylnonamethylcyclopentasiloxane (II), and bis(γ-trifluoropropenyl)-hexamethylcyclotetrasiloxane (III), their purity established by gas-liquid chromatography. The physical constants of the oligomers obtained are given in Table 1. The presence of a double bond in I–III was established qualitatively by their decoloration of bromine water.

The IR spectra of I, II, and III exhibit strong absorption bands, respectively, in the 1040–1020, 1090–1040, and 1100–1080 cm^{-1} regions corresponding to the vibrations of Si—O—Si in six-, ten-, and eight-membered cyclosiloxanes. The bands in the 825–810 and 1280–1273 cm^{-1} regions show the presence of $Si—CH_3$ groups, and those at 1270—1230 cm^{-1} the presence of a CF_3 group. The spectra have no absorption in the region of double bonds but have a doublet at 3050–3018 cm^{-1} which is characteristic for the stretching vibrations of C—H in the —HC═CH— skeleton [21].

In all syntheses, after the organocyclosiloxanes had been distilled off, a considerable amount of still residue (50%) remained. High-vacuum distillation of the still residues (at $4 \cdot 10^{-3}$ mm) did not suceed in yielding individual substances. When the fractions isolated from the still residue were redistilled, 60% of them was converted into a gel-like polymer very sparingly soluble in ether.

The organocyclosiloxanes synthesized were subjected to polymerization in the presence of 0.1–4 wt. % of benzoyl peroxide or azoisobutyronitrile.

However, even on prolonged (35 hr) heating of the mixture of oligomers and catalyst in sealed tubes from which the air had previously been pumped out, with simultaneous irradiation with ultraviolet light, no polymeric products were obtained.

The use of a Ziegler-Natta catalyst led to oily polymeric compounds with molecular weights of from 1000 to 3000 which were sparingly soluble in benzene and other organic solvents.

EXPERIMENTAL

The syntheses were carried out with dimethyldichlorosilane having bp 70°–71° C, n_D^{20} 1.4002 (54.3% Cl) and with γ-trifluoropropenylmethyldichlorosilane having bp 107° C, n_D^{20} 1.3888 (34.1% Cl).

The cohydrolysis reaction. At 70°–75° C, a solution of 108.9 g (0.52 mole) of γ-trifluoropropenylmethyldichlorosilane and 74 g (0.57 mole) of dimethyldichlorosilane in 180 g of toluene was slowly added to the aqueous layer of a mixture of 180 g of distilled water and 180 g of toluene. After this, the reaction mixture was stirred for another 30 min and cooled, and the organic layer was separated off, washed with water to neutrality, and dried with $CaCl_2$. The

Table 1

Characteristics of the Oligomers obtained

Compound	Bp, °C (pressure, mm)	n_D^{20}	d_4^{20}	MR_D	
				found	calculated
I	52—56	1.3800	1.0804	64.78	65.02
II	65—70	1.3850	1.0353	102.00	102.42
III	98—103	1.3970	0.9535	115.30	116.01

Table 2

Polymerization of I and II in the Presence of Ziegler–Natta catalyst

Initial oligomer	Amount, g	Molar ratio of catalyst to monomer	Molar ratio of $Al(C_2H_5)_3$ to $TiCl_4$	Yield of polymer, g	*M**
I	5.3	1 : 1	0.096 : 0.156	1.71	3040
II	4.8	1 : 1	0.0863 : 0.1430	1.69	1050

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*Determined cryoscopically in octamethylcyclotetrasiloxane.

toluene was distilled off in a vacuum of 30 mm. This gave 95.2 g of reaction product from which 47.4 g of a fraction with bp 50°–118° C was distilled off. Two redistillations in vacuum through a column gave: 9.9 g (21%) of I. Found, %: C 31.68, 31.76; H 5.31, 5.37; Si 27.61, 27.63; F 19.19, 18.75; Mol. wt. 306.4. Calculated for $C_8H_{17}O_3Si_3F_3$, %: C 31.77; H 5.75, Si 27.83; F 18.84; Mol. wt. 302.4. 5.3 g (11.2%) of II. Found, %: C 31.91, 32.12; H 6.30, 6.34; Si 30.60, 30.03; F 11.95, 11.99; Mol. wt. 448. Calculated for $C_{12}H_{29}O_5Si_5F_3$, %: C 31.98; H 6.48; Si 31.13; F 12.64. Mol. wt. 450.6. 2.7 g (5%) of III. Found, %: C 31.70; H 4.71; Si 24.05; 24.15; F 25.77 Mol. wt. 450. Calculated for $C_{12}H_{22}O_4Si_4F_6$, %: C 31.56; H 4.85; Si 24.80; F 24.99. Mol. wt. 456.6.

Polymerization of the organocyclosiloxanes. The polymerization apparatus was evacuated to a residual pressure of 1–2 mm, and then was filled to atmospheric pressure with dry argon (this operation was repeated four times). Triethylaluminum was added to the apparatus from a Schlenk vessel and with vigorous stirring titanium tetrachloride was introduced. This gave a finely disperse powder. The monomer was added to the mixture obtained, and the whole was heated at 85°–90° C with stirring for 27 hr and was then poured into methanol saturated with hydrogen chloride. The polymer that deposited was separated from the catalyst residues by decantation, dissolved in benzene with gentle heating, purified by reprecipitation from methanol, and dried in vacuum at 30° C to constant weight (Table 2).

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