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Polymerization of N-Phenylcyclosilazoxanes

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ABSTRACT

Anionic polymerization of six-membered N-phenylcyclosilazoxanes (I and II) was attempted, but only an equilibrium mixture of oligomeric cyclic and linear silazoxanes was formed. On the other hand, anionic copolymerization of the cyclosilazoxanes with hexamethylcyclotrisiloxane in various proportions yielded high molecular weight polysilazoxanes. The polymers are viscous liquids of high thermal stability (up to 500°C).

INTRODUCTION

The products of polymerization of linear and cyclic silazanes have been shown to have remarkable thermal stability (up to 500°C) [1-3]; however, their general usefulness is limited by their low resistance to hydrolysis and their highly crosslinked, polycyclic structure [4, 5]. The latter property is responsible for the brittleness, hardness, and comparatively high glass transition temperatures of these materials. Attempts to prepare linear polysilazanes of high molecular weight failed because of the tendency of the silazane chain to rearrange with formation of cyclic compounds [6-8]. The products of polymerization were viscous liquids of low molecular weight (800-1200).

Since siloxanes are known to form long chains of high stability, we have investigated the possibility of preparing linear, thermostable polysilazoxanes, i.e., polymers containing both silazane and siloxane units in the main chain. Murray [9] claimed to have prepared linear polymers of high molecular weight and regular structure from cyclosilazoxanes $[(CH_3)_2Si]_3O_2NH$ and $[(CH_3)_2SiOSi(C_6H_5)_2OSi(CH_3)_2NH]$ in the presence of basic catalysts Me_4NOH or KOH-Me_2SO and a solution of iodine in benzene. We have previously prepared two new N-phenylcyclosilazoxanes [10]: $[(CH_3)_2Si]_3O_2NC_6H_5$ (I) and $[(CH_3)_2Si]_3O(NC_6H_5)_2$ (II). The present paper is concerned with attempts to polymerize them in the presence of anionic catalysts and also with their anionic copolymerization with hexamethylcyclotrisiloxane.

RESULTS AND DISCUSSION

Preliminary attempts to prepare linear silazoxane polymers by reacting compound I or II with polysiloxanediols $HO[Si(CH_3)_2O]_nH$ (n = 2, 4, 5) failed. No reaction took place in boiling toluene with amines as catalysts. On the other hand, in dimethyl sulfoxide with a potassium polysiloxanediolate catalyst at 100° C or in bulk, without catalyst at 180° C, a polysiloxane polymer and aniline from decomposition of the silazoxane ring were the only products.

Attempts to polymerize I and II were carried out in bulk with various concentrations of catalyst–potassium polysiloxanediolate at 120-180° C, at normal pressure under nitrogen or in vacuo (10^{-3} Torr). Compounds I and II were found to polymerize under these conditions (II with the addition of DMSO as activator only). Since potassium siloxanediolate is known to be an active catalyst for siloxane polymerization, the initiation step is obviously similar in the present case and the siloxane linkage is first broken.

The reaction, however, did not yield high molecular weight polymers. The liquid products were shown by infrared and PMR spectra and elemental analysis to be polysilazoxanes with molecular weights (osmometric), depending on the reaction conditions, from 1000 to 6500, corresponding to a degree of polymerization of 3 to 20 or a content of SiO and SiNPh units from 9 to 60. The reaction reaches an equilibrium, and the final yield of polymeric material is seldom higher than 50%. The other compounds at equilibrium are crystalline

TABLE 1. Polymerization of N-Phenylcyclosilazoxanes I and II

Monomer	Atmosphere	Temp (°C)	Reaction time (hr)	Catalyst concn (calcd as Si:K)	DMSO added	Polymer yield (%)	Silazoxane in product (wt %)		Elemental analysis found[a]				Molecular weight
							I	II	Si (%)	C (%)	H (%)	N (%)	
I	N_2	140	20	1200	–	78	b	b	27.8	44.87	7.64	4.19	6500
I	N_2	130	42	1200	–	42.5	–	6.5	28.64	41.58	7.60	4.11	500
I	N_2	130	26	1300	–	25.6	–	40.0	28.59	40.01	8.10	3.18	1000
II	N_2	130	50	1250	–	–	–	98	21.50	57.95	7.50	7.50	–
I	N_2	100-130	14	1300	+	48	16	–	28.28	45.37	7.77	4.34	2000
II	N_2	130	50	1300	+	84	–	10	22.81	48.70	7.84	5.46	700
I	vac	130	50	1300	+	26.2	48.5	–	29.04	41.81	7.87	3.31	1200
I	vac	140	20	2400	–	–	96	–					–
I	vac	140	13	1000	–	22	c	c	28.50	36.00	4.54	3.58	600
I	vac	140	56	500	–	23.4	34.5	29	33.40	40.51	7.43	3.55	1100

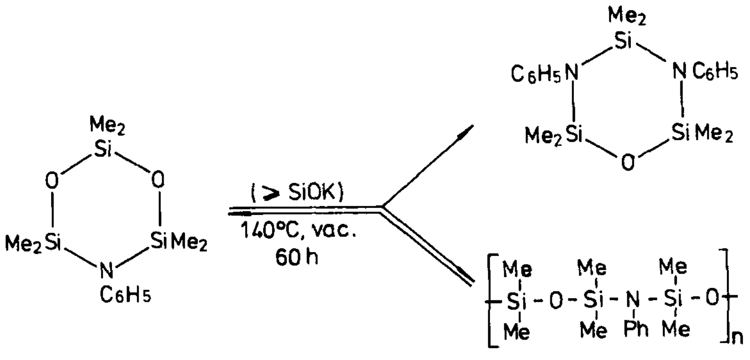
[a] Calculated for I: Si, 28.32%; C, 48.43%; H, 7.79%; N, 4.71%. Calculated for II: Si, 22.61%; C, 58.01%; H, 7.57%; N, 7.52%.

[b] 20% crystalline material.

[c] 40% crystalline material.

and in the case of the polymerization of I, compound II was found, by elemental and spectroscopic analysis, as well as by mixed melting point with an authentic sample, to be one of the major components of the mixture (Table 1).

The growth of the polymer chain is thus inhibited by rearrangements involving formation of six-membered silazoxane rings. These small rings are thermodynamically favored in their equilibrium with linear polysilazoxanes. The general scheme of the reaction can be represented by Eq. (1).



(1)

In a series of experiments dimethyl sulfoxide (5% by weight of monomer) was added as activator of polymerization; a remarkable acceleration of the reaction was observed, and the yield of the polymer was increased but the molecular weight remained low (Table 1).

Elemental analysis of the polymers showed that the proportions of carbon and nitrogen were lower than in the monomers. It can be concluded therefrom that some silazane linkages are also broken during the reaction and some nitrogen is lost, probably as aniline (evaporating with other volatile materials from the reaction product, see Experimental Section). The polymers thus become richer than the monomer in siloxane units.

The infrared and PMR spectra of the polymers are very similar to those of the monomers. In the IR spectrum two split bands at 900, 910 and 975, 995 cm^{-1}, characteristic of Si–N–Si vibrations, are observed. There is also a broad Si–O–Si band at 1100-1030 cm^{-1} and a series of bands attributed to vibrations of the benzene ring at 700, 1220, 1500, 1610, and 3060 cm^{-1}.

In the PMR spectra of some of the polymers, instead of the expected two singlets (δ 0.57 and 0.72 ppm) corresponding to methyl protons of $-O-Si(Me_2)-N-$ and $-O-Si(Me_2)-O-$ and a multiplet (δ 5.9-6.25 ppm) of the aromatic protons, three singlets (δ 0.49, 0.65, and 0.77 ppm) and two multiplets (δ 5.6-5.85 ppm and 5.9-6.22 ppm) were observed. It seems possible that, in addition to isolated silazane units, some sequences of them can also occur in the polymer chain, which would give two additional signals in the PMR spectrum arising from $-(Ph)N-Si(Me_2)-N(Ph)-$.

In order to prepare high molecular weight silazoxane polymers, we further attempted to copolymerize the cyclosilazoxanes I and II with cyclosiloxanes. Copolymerization of I with hexamethylcyclotrisiloxane (D_3) proved successful [Eq. (2)]. The polymerizations were carried out in bulk with potassium polysiloxanediolate as catalyst, at 130°C in vacuo (10^{-3} Torr). The polymers prepared in this way have high molecular weights whose values depend on the molar ratio of comonomers in the starting material and on the resulting composition of the copolymer (Fig. 1). The viscosity and molecular weight decrease with the increase of the number of silazane units in the copolymer chain.

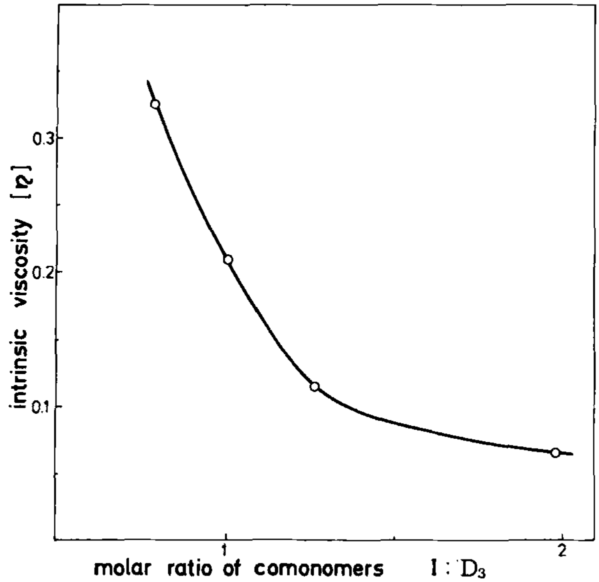


FIG. 1. Effect of increasing the proportion of silazane units on the molecular weight of a silazoxane polymer.

TABLE 2. Copolymerization of N-Phenylcyclosilazoxanes I and II with Hexamethylcyclotrisiloxane (D_3)[a]

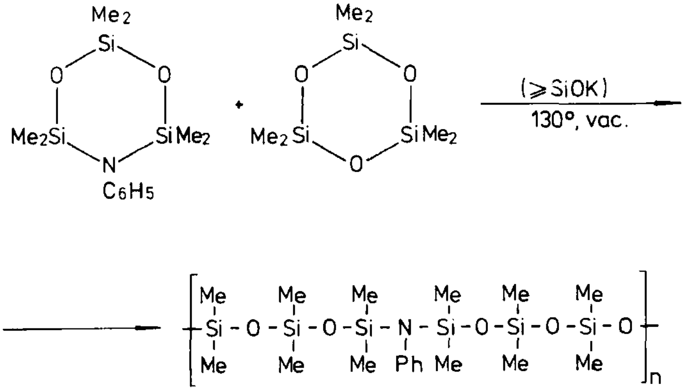
	Molar ratio I:D_3		Yield	Elemental analysis of copolymer				Nature of		Thermal
	In monomer	In polymer	(%)	Si (%)	C (%)	H (%)	N(%)	volatile product	$\overline{M}_n$	stability (°C)[b]
1	1:1	1:1	64	32.48	41.30	7.99	2.80	I and II	80,000	570
2	2:1	1.25:1	63	31.56	43.04	8.41	2.94	"	15,000	570
3	1.25:1	1.25:1	69	31.71	42.48	7.72	3.06	"	18,000	540
4	0.8:1	0.8:1	82	33.13	40.54	8.28	2.71	"	73,000	540
5	II:D_3 = 1:1[c]									

[a] Polymerization in bulk; catalyst solution of potassium siloxanolate in n-heptane; Si:K = 2000; $p = 10^{-3}$ Torr; T = 130° C.

[b] The temperature of maximum rate of weight loss (highest peak on the DTG curve) was taken as the measure of thermal stability.

[c] At 130-190° C the product was a siloxane polymer + unreacted II.

For example, the reaction of I with D_3 in equimolar proportion yielded a highly viscous liquid with a number-average molecular weight $\overline{M}_n$ of 80,000. When the molar ratio of I to D_3 was increased to 1.25 the copolymer had $\overline{M}_n$ = 18,000 only (Table 2). Increasing the molar ratio of I to D_3 to more than 1.25 did not result in further increase of the proportion of silazane units in the copolymer (Table 2).



(2)

In the IR spectra of the copolymers all the expected bands are present: Si–N–Si, split bands at 895, 910 and 975, 985 cm^{-1}; Si–O–Si, broad band at 1100-1020 cm^{-1}; benzene ring at 700, 1220, 1500, 1600, and 3050 cm^{-1}.

The PMR spectra contain the following signals: low intensity singlet at δ 0.55 ppm, corresponding to methyl protons of $-(Ph)N-Si(Me_2)-O-$; high intensity singlet at δ 0.60 ppm assigned to methyl protons of $-O-Si(Me_2)-O-$; a multiplet at δ 5.9-6.3 ppm for phenyl protons.

The silazoxane polymers are clear, highly viscous liquids resembling linear polysiloxanes; however, their thermal stability is much higher (Figs. 2-4). Polysiloxanes suffer substantial weight loss at 300° C, whereas the polysilazoxanes show fast weight loss only at 500° C or even higher temperatures. The heat resistance of the polysilazoxanes does not appear to depend much on the proportion of silazane units in the macromolecule.

The high thermal stability of these polymers cannot be due to the strength of the silazane bond, as the energy of this bond is lower than that of Si–O. It may be that the presence of silazane unit, by

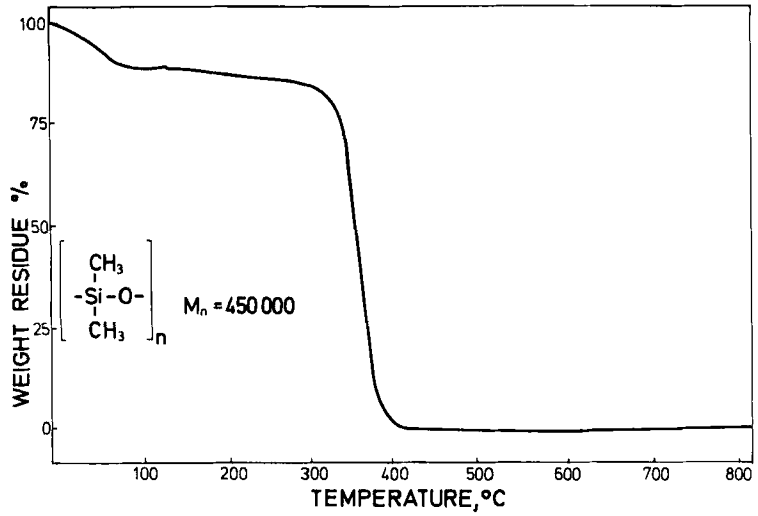


FIG. 2. Thermal behavior of a polysiloxane. Heating rate, 7.9° C/min; atmosphere, nitrogen.

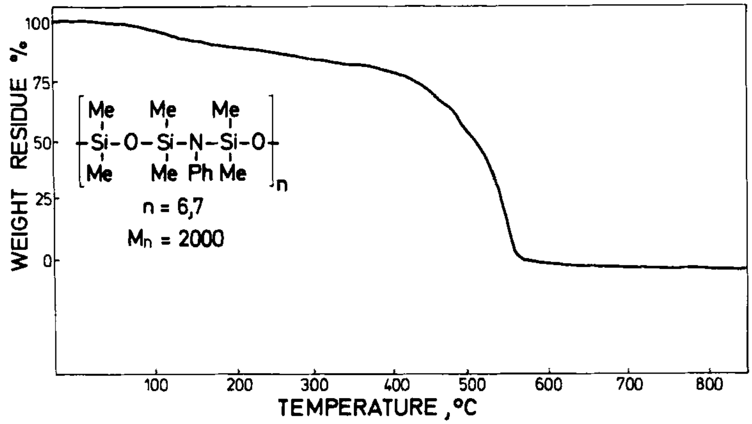


FIG. 3. Thermal behavior of a polymer formed from cyclosilazoxane I. Heating rate, 7.9° C/min; atmosphere, air.

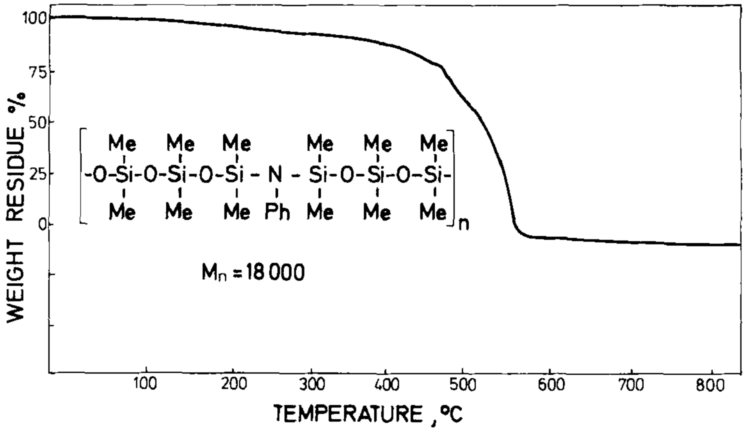


FIG. 4. Thermal behavior of a copolymer from cyclosilazoxane I and hexamethylcyclotrisiloxane in a 1:1 molar proportion. Heating rate, 7.9° C/min; atmosphere, air.

disturbing the regular structure of the siloxane chain, prevents the occurrence of intramolecular reactions which are responsible for the depolymerization and formation of small, volatile rings.

EXPERIMENTAL

Monomers

Compounds I and II were prepared by condensation of aniline with 1,5-dichlorohexamethyltrisiloxane (preparation of I) or with 1,3-dichlorotetramethyldisiloxane and dichlorodimethylsilane (preparation of II) [10].

I was repeatedly sublimated and dried on a vacuum line. II was dried on the vacuum line for over 10 hr. Hexamethylcyclotrisiloxane (D_3) prepared by pyrolysis of methylsilicone oil was distilled three times through a column, dried by fusing with CaH_2, and distilled from CaH_2 and NaH in vacuo.

Catalyst and Activator

Octamethylcyclotetrasiloxane (D_4) was equilibrated with KOH in n-heptane under nitrogen to yield potassium polysiloxanediolate. This was stored in small glass ampoules sealed on the vacuum line and used as catalyst for polymerizations and copolymerizations of N-phenylcyclosilazoxanes as a solution in n-heptane containing 0.299 mmole K/g.

Dimethyl sulfoxide (activator) was distilled at reduced pressure under nitrogen from CaH_2.

Polymerization of N-Phenylcyclosilazoxanes

The conditions of polymerizations are given in Table 1. Reactions were carried out at atmospheric pressure under nitrogen in a flask equipped with a stirrer, thermometer, reflux condenser, and nitrogen inlet tube. After an appropriate time the reaction was quenched by cooling the flask and adding chlorotrimethylsilane in a tenfold molar excess over the amount of potassium in the catalyst used. Stirring was continued for 1 hr at room temperature, and the volatile compounds were evaporated by heating the product for 10 hr at 0.1 Torr, then at 10^{-3} Torr (vacuum line) at 130-140°C.

Polymerizations at reduced pressure were carried out in the same way as the copolymerizations described below.

Copolymerizations of N-Phenylcyclosilazoxanes with Hexamethylcyclotrisiloxane

The conditions of the reactions are given in Table 2. All the reactions were carried out in an ampoule at 10^{-3} Torr in the following way. A vial containing the catalyst and a break-seal were placed in a thick-walled tube terminated by a constriction. Another vial with DMSO distilled into it on the vacuum line was also placed in the tube in cases of polymerization carried out with activator. The tube was sealed and evacuated thoroughly on the vacuum line. The comonomers were distilled in, and the tube was evacuated again and separated from the line by sealing at the constriction. The ampoule was heated in an oil bath to melt the monomers, the vial with the catalyst (and activator) was broken, and the contents were thoroughly mixed together. The ampoule was put again into the oil bath and the reaction was carried out until the mixture became highly viscous. After cooling, the reaction was quenched with chlorotrimethylsilane. The polymer was heated on the vacuum line until free from volatile compounds.

Characterization and Spectra

The infrared spectra were taken on films with a Unicam SP 1200-S spectrometer.

The PMR spectra were measured in CCl_4 with CH_2Cl_2 as internal standard on a Tesla BS 487C spectrometer at 80 MHz.

Number-average molecular weights were determined on Knauer vapor-pressure osmometer in benzene.

Thermogravimetric analyses were carried out by using a Paulik, Paulik, Erdey thermobalance.

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