Reports of the Academy of Sciences of the USSR

Corresponding Member of the Academy of Sciences of the USSR N. S. NAMETKIN, V. M. VDOVIN,

1965

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR

1965. Volume 162, No. 4

CHEMISTRY

Corresponding Member of the Academy of Sciences of the USSR N. S. NAMETKIN, V. M. VDOVIN,
V. I. ZAVYALOV

POLYMERIZATION

OF 1,1,3,3-TETRAPHENYL-1,3-DISILACYCLOBUTANE

As a result of carrying out thermal or catalytic polymerization of monosilacyclobutanes ([1,2]), up to the present study we obtained high-molecular-weight products with comparatively low glass-transition temperatures. Some polymers of this type were crystalline substances with low melting points. For example, polymers of 1,1-diphenyl-, 1,1-dimethyl-, and 1-methyl-1-phenylsilacyclobutanes have the following properties (Table 1).

Table 1

Polymer	Intrinsic viscosity in benzene (100 ml/g)	Structure (X-ray data)	T_g^*	M.p. **
$\left[\begin{array}{c}CH_3\\ SiCH_2CH_2CH_2\\ CH_3\end{array}\right]_n$	2.58	cryst.	−70°	+40°
$\left[\begin{array}{c}CH_3\\ SiCH_2CH_2CH_2\\ C_6H_5\end{array}\right]_n$	2.49	amorph.	−30°	–
$\left[\begin{array}{c}C_6H_5\\ SiCH_2CH_2CH_2\\ C_6H_5\end{array}\right]_n$	2.30	cryst.	–	+55°

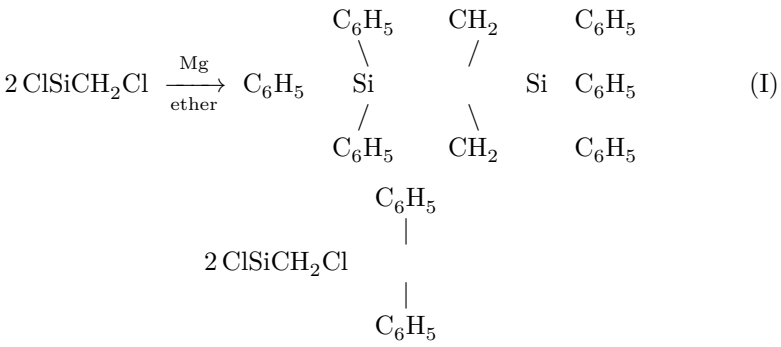
* The glass-transition temperature was determined by Marey' s method.
** The melting point was determined in a polarizing microscope.

Fig. 1. X-ray diffraction pattern of the polymer of 1,1,3,3-tetraphenyl-1,3-disilacyclobutane

Figure 1: Fig. 1. X-ray diffraction pattern of the polymer of 1,1,3,3-tetraphenyl-1,3-disilacyclobutane

In the present work we have shown that by polymerization of four-membered silicon–carbon heterocycles it is also possible to obtain a high-molecular-weight product with a high melting point.

As the monomeric compound we used 1,1,3,3-tetraphenyl-1,3-disilacyclobutane, obtained according to scheme ([3]) (I), see Table 2.



(I)

The product, purified by repeated recrystallizations from ether and benzene, was dried and freed from occluded air in a vacuum of 10^{-4} mm Hg, after which ampoules with the evacuated monomer were heated at 180–200° for 2–4 hours. During heating, the polymer formed precipitated from the monomer solution, and after only 2–4 hours the polymer yield reached 85%.

In contrast to the previously obtained polymers from mono- and disilacyclobutanes, polymeric 1,1,3,3-tetraphenyl-1,3-disilacyclobutane did not dissolve in ordinary organic solvents. Therefore, liberation

To the article by N. S. Nametkin, V. M. Vdovin, and V. I. Zavyalov, p. 824

Fig. 1. X-ray diffraction pattern of the polymer of 1,1,3,3-tetraphenyl-1,3-disilacyclobutane

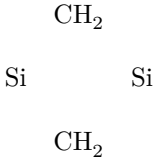
the polymer from the monomer, which is readily soluble in benzene (and, possibly, other low-molecular-weight products), was carried out by treating the reaction products with boiling benzene. The degree of purification was monitored by IR analysis from the disappearance in the spectra of the reaction products of the band at 930 cm^{-1}, characteristic ([3]) of

Fig. 2. IR spectrum of the polymer

Figure 2: Fig. 2. IR spectrum of the polymer

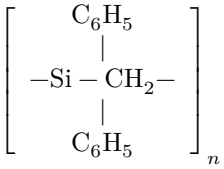
Fig. 3. IR spectrum of the monomer

Figure 3: Fig. 3. IR spectrum of the monomer



groups of the monomers, and also by the absence on the thermogram (differential thermal analysis on a Kurnakov apparatus) of the endothermic peak characterizing melting of the monomer. The elemental composition of the purified polymer corresponded to the monomer; the product was a white powder, soluble in boiling dicumylmethane and precipitating on cooling of the solution below 250°.

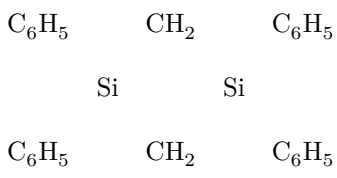
Fig. 2. IR spectrum of the polymer



According to X-ray structural analysis (Fig. 1), the substance obtained has a crystalline structure; in the field of a polarizing microscope, at 600-fold magnification, crystallites of the polymer are clearly visible. The substance melts at 340°, and the melting temperature of the sample is reproduced many times; it also does not change after precipitation of the polymer from solution in dicumylmethane.

The structure of the polymer was established on the basis of comparison of the spectra of the polymer (Fig. 2), the monomer (Fig. 3), and a specially synthesized model individual compound containing the groupings $C_6H_5Si \equiv$ and an unstrained chain $\equiv SiCH_2Si \equiv$. The model compound was prepared by us by method ([4]) according to scheme (II) and was isolated by recrystallizations (from chloroform and ether)

Fig. 3. IR spectrum of the monomer



$$[\text{II}]\quad \mathrm{ClCH_2Cl} \xrightarrow{\mathrm{Si/Cu}} \mathrm{Cl_3SiCH_2SiCl_3} \xrightarrow{\mathrm{LiC_6H_5}} \rightarrow (\mathrm{C_6H_5})_3\mathrm{SiCH_2Si}(\mathrm{C_6H_5})_3$$

from the fraction with b.p. 300–350°/3 mm.

When the spectra of the monomer and polymer are compared, it is seen that in the latter the characteristic frequency of 1,3-disilacyclobutanes is absent. At the same time, the spectra of the polymer and the model differed practically only in the ratio of the intensities of the bands characterizing methylene groups and phenyl rings.

Thus, 1,1,3,3-tetraphenyl-1,3-disilacyclobutane, like other silacyclobutane derivatives, polymerizes according to scheme (III).

$$[\text{III}]\; n \quad \mathrm{C_6H_5}\!\!\begin{array}{c}\mathrm{C_6H_5}\\ \backslash\\ \mathrm{Si}\\ /\\ \mathrm{C_6H_5}\end{array}\!\!\mathrm{CH_2}\!\!\begin{array}{c}\mathrm{C_6H_5}\\ \backslash\\ \mathrm{Si}\\ /\\ \mathrm{C_6H_5}\end{array}\!\!\mathrm{CH_2} \xrightarrow{t^\circ} \left[\begin{array}{c}C_6H_5\\ |\\ SiCH_2\\ |\\ C_6H_5\end{array}\right]_{2n}$$

In the present work we also established the possibility of carrying out catalytic polymerization of 1,1,3,3-tetraphenyl-1,3-disilacyclobutane in solutions, at temperatures of 20–100°, in the presence of soluble catalysts—silanolates of alkali metals. In particular, polymerization of 1,1,3,3-tetraphenyl-1,3-disilacyclobutane proceeds in benzene solution at temperatures of 60–80° with 2–20 mole % potassium phenyldimethylsilanolate and, as in the case of thermal polymerization, a polymer with a silylmethylene main chain is formed.

Table 2

Substance	Mol. wt.* found	Mol. wt.* calculated	M.p., °C**	Found, % Si	Found, % C	Found, % H	Calculated, % Si	Calculated, % C	Calculated, % H
$(C_6H_5)_3SiCH_2Si(C_6H_5)_3$	561	572.7	141.8–142.5	10.70	83.5	6.29	10.53	83.41	6.05

Substance	Mol. wt.* found	Mol. wt.* calculated	M.p., °C**	Found, % Si	Found, % C	Found, % H	Calculated, % Si	Calculated, % C	Calculated, % H
$(C_6H_5)_3SiCH_2Si(C_6H_5)_3$	508	532.7	141.8–142.5	10.46	83.3	6.21	10.53	83.41	6.05
$[-Si(C_6H_5)_2CH_2-]_n$	340			14.45	79.15	6.10	14.29	79.54	6.17
$[-Si(C_6H_5)_2CH_2-]_n$	340			14.71	79.50	6.16	14.29	79.54	6.17
$(C_6H_5)_2Si(CH_2)_2Si(C_6H_5)_2$	396	394.6	121–122	14.26	79.43	6.27	14.29	79.54	6.17
$(C_6H_5)_2Si(CH_2)_2Si(C_6H_5)_2$	396	394.6	121–122	14.40	79.43	6.35	14.29	79.54	6.17

* By the cryoscopic method in benzene.
** In a capillary.

The IR spectra of the products obtained were recorded in potassium bromide pellets on a UR-10 spectrophotometer in the laboratory of physicochemical methods of investigation of the A. V. Topchiev Institute of Petrochemical Synthesis, Academy of Sciences of the USSR, by V. D. Oppengeim.

The X-ray diffraction pattern of the polymer was recorded on a URS-60 X-ray unit with CuKα radiation in the group for physicochemical investigations of high-molecular compounds by I. A. Litvinov.

The authors express their gratitude to V. D. Oppengeim and I. A. Litvinov for the work performed.

A. V. Topchiev Institute of Petrochemical Synthesis
Academy of Sciences of the USSR

Received
17 X 1964

CITED LITERATURE

1. N. S. Nametkine, V. M. Vdovine, *J. Polym. Sci.*, part C, No. 4, 1043 (1963).

2. N. S. Nametkin, V. M. Vdovin, V. I. Zavyalov, *Izv. AN SSSR, OKhN*, 1964, No. 1.

3. N. S. Nametkin, V. M. Vdovin et al., *Izv. AN SSSR, ser. khim.*, 1965, No. 5.

4. N. S. Nametkin, A. V. Topchiev, V. I. Zetkin, *DAN*, 87, 59 (1952).

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