AMMONOLYSIS OF 1,4-BIS(DIMETHYLCHLOROSILYL)BENZENE

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Khimiya Geterotsiklicheskikh Soedinenii, Vol. 4, No. 3, pp. 554–556, 1968

UDC 547.898+547.79'128:542.952.6

The ammonolysis of 1,4-bis(dimethylchlorosilyl)benzene with ammonia forms heterocyclic compounds of low molecular weight. The main reaction product is the crystalline $[CH_3)_2SiC_6H_4Si(CH_3)_2NH]_4$, which polymerizes on heating with the formation of polymers possessing a relative viscosity of 0.15–0.4.

There is no information in the literature on the amination of halogen derivatives of disilylbenzenes.

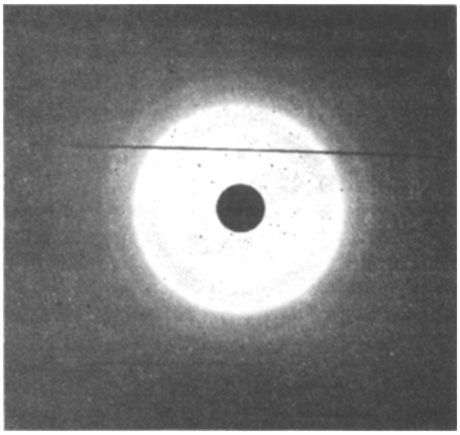
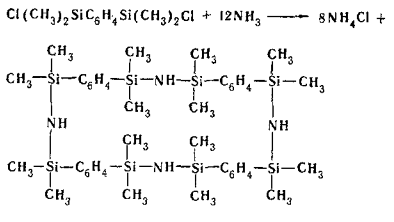


Fig. 1. X-Ray diagram of III with η 0.18.

A study of the ammonolysis of 1,4-bis(dimethylchlorosilyl)benzene (I) has shown that the action of gaseous NH_3 on its solutions does not lead to the formation of high-molecular-weight compounds, as was to be expected: comparatively low-molecular-weight crystalline substances are always obtained. Changing the reaction temperature (from −40 to 0° C), the solvent (benzene, toluene, ether), and replacing the gaseous ammonia by liquid ammonia had no effect on the direction of the process. In all cases a crystalline compound with mp 129–130°C was isolated (yield 91.6%). The analytical data and determinations of the molecular weight ebullioscopically (780) and cryoscopically (870) have shown that it corresponds to the formula $[CH_3)_2SiC_6H_4Si(CH_3)_2NH]_4$ (II), i.e., the ammonolysis reaction takes place in the following way:



$$Cl(CH_3)_2SiC_6H_4Si(CH_3)_2Cl + 12NH_3 \longrightarrow 8NH_4Cl +$$

No cyclic compounds with a smaller number of links in the ring were found in the products of the ammonolysis of I, which is undoubtedly due to the considerable rigidity of the $—Si—C_6H_4—Si—$ grouping. Nevertheless, the presence of an NH group between the $—Si—C_6H_4—Si—$ groups probably ensures sufficient flexibility of the chain to shift the reaction in the direction of the predominant formation of cyclic, and not linear, compounds. This apparently also explains why linear polymers are not formed in the direct ammonolysis of I.

It appeared of interest to investigate the possibility of converting II into compounds of high molecular weight. Its thermal polymerization at 150, 200, and 250° C in the presence of traces of NH_4Cl showed that II is converted relatively easily into an elastic polymer (III) while its reduced viscosity varies from 0.15 to 0.4 according to the time and conditions of the condensation process. Compound III has a well-expressed ordered structure, as can be seen from its X-ray diagram (Fig. 1).

The elementary composition of III at the end of polymerization is the same as that of compound II. This shows that the process takes place through the opening of the ring. The thermomechanical properties of III, which are illustrated in Fig. 2, show that the glass temperature changes according to the magnitude on $[\eta]$ and shifts in the direction of positive temperatures when $[\eta]$ increases. Compound III is soluble in dimethylformamide, tetrachloroethane, and pyridine, and is insoluble in benzene, toluene, ethyl ether, chloroform, and petroleum ether but swells in these solvents.

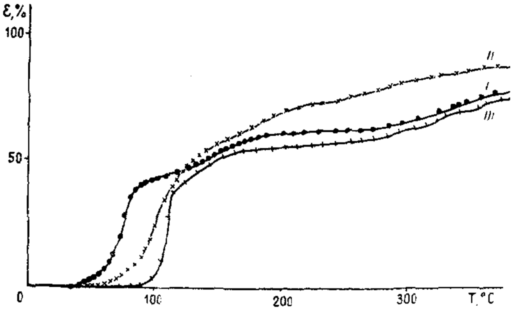


Fig. 2. Thermomechanical curves of III obtained by the polymerization of II: 1) 150° C, 3 hr; 2) 200° C, 3 hr; 3) 250° C (3–4 mm), 3 hr.

EXPERIMENTAL

Ammonolysis of p-$[Si(CH_3)_2Cl]_2C_6H_4$ with gaseous ammonia. A four-necked flask fitted with a stirrer, thermometer, reflux condenser, and tube for the introduction of ammonia was charged with 26.3 g (0.1 mole) of I and 260 ml of dry toluene. Dry ammonia was passed through the solution at −5 to 0° C for 4 hr. The precipitate was separated off and washed with toluene. The solvent was distilled off from the filtrate at room temperature and a pressure of 20–25 mm.

This gave 20.3 g (98%) of a white pulverulent substance. After recrystallization from a threefold amount of hot hexane, dry pyridine, or tetrachloroethane, 18.6 g (91.6%) of II was obtained in the form of white acicular crystals with mp 129–130° C. Found, %: C 57.78, 58.08; H 8.17, 8.34; Si 26.98, 27.18; N 7.14, 6.98; mol. wt. 870 (cryoscopically in benzene), 780 (ebullioscopically in benzene). Calculated for $C_{40}H_{68}Si_8N_4$, %: C 58.00; H 8.22; Si 27.08; N 6.75; mol. wt. 828.

Ammonolysis of p-$[Si(CH_3)_2Cl]_2C_6H_4$ with liquid ammonia. A four-necked flask fitted with a stirrer, theremometer, reflux condenser, and tube for the introduction of ammonia was charged with 200 ml of dry toluene and, with cooling to ~ −45° C, ammonia was passed in for 1 hr. Then, at the same temperature, a solution of 26.1 g (0.1 mole) of I in 60 ml of toluene was added dropwise over 30 min. Stirring and the passage of ammonia were continued for another 2 hr 30 min. After the mixture had reached room temperature, the precipitate was separated off and the filtrate was evaporated in vacuum to constant weight at 20° C (2–3 mm). This gave 20.9 g of I (white crystalline powder). Found, %: C 57.08, 57.62; H 8.10, 8.18; Si 27.06, 27.05; N 6.76, 6.91.

Polymerization of II. Test-tubes each containing 1 g of II were placed in a thermostated vessel at 100, 200, or 250° C. In 10–15 min, the II was converted into a highly elastic polymer (III). The specific viscosity of the 1% solution of III in dimethylformamide was 0.1–0.14 in all experiments and did not increase when heating was carried out for 6–8 hr.

Polymerization in vacuum was carried out at 2–3 mm and temperatures of 200, and 250° C. Before being placed in the thermostated vessel, the test-tube was filled with ammonia. On polymerization at 200° C, η_{sp} of a 1% solution of III in dimethylformamide was 1.8 after 3 hr and had not changed after 6 hr. On polymerization at 250° C, η_{sp} was 0.38 after 3 hr and 0.4 after 6 hr. The reduced viscosity of III was 0.34. Semitransparent brittle films were obtained from a solution of III. Found, %: C 58.51, 58.13; H 8.41, 7.98; Si 26.33, 26.78; N 6.76, 6.91. Calculated for $C_{10}H_{17}Si_2N$, %: C 52.00; H 8.22; Si 27.08; N 6.75.

The IR spectrum of II has a strong absorption band at 3340 cm^{-1} corresponding to a N—H bond and also bands corresponding to a CH_3—Si bond (800, 1260, 2900, 2960 cm^{-1}) and a $-C_6H_4-$ group (1140, 3050 cm^{-1}).

27 July 1965

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for Plastics, Moscow