1,1,2,2-Tetramethyl-3-trimethylsilyl-1,2-disilacyclobutane: synthesis and spontaneous polymerization

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Gas-phase dehalogenation of 1,2-bis[chloro(dimethyl)silyl]-2-trimethylsilylethane with alkali metals gave 1,1,2,2-tetramethyl-3-trimethylsilyl-1,2-disilacyclobutane (**3**). Its spontaneous ring-opening polymerization at room temperature afforded an amorphous linear polymer with $T_g = -8.9 \,^{\circ}$ C, $M_w = 3.47 \cdot 10^5 - 3.85 \cdot 10^5$, and $M_w/M_n = 2.43 - 2.86$. According to spectroscopic data (IR and ¹H, ¹³C, and ²⁹Si NMR), the backbone of the polymer consists of alternating monomer units joined in the "head-to-tail" ([Me_2SiCH(SiMe_3)CH_2SiMe_2SiMe_2CH-(SiMe_3)CH_2SiMe_2]) and "head-to-head" ways ([Me_2SiCH_2CH(SiMe_3)SiMe_2SiMe_2CH-(SiMe_3)CH_2SiMe_2]).

Key words: 1,1,2,2-tetramethyl-3-trimethylsilyl-1,2-disilacyclobutane, spontaneous polymerization, organosilicon compounds.

The lower homologs of the 1,2-disilacyclobutane (1,2-DSCB) series are highly reactive and not easily accessible. The synthesis and study of these monomers were made possible by development of gas-phase dehalogenation of 1,2-bis[chloro(dimethyl)silyl]ethane with the alkali metal vapors, which allows stabilization of the resulting 1,1,2,2-tetramethyl-1,2-disilacyclobutane (1) in a trap cooled to 77 K. When kept at room temperature, compound 1 undergoes spontaneous exothermic ring opening via homolytic cleavage of the Si-Si bond followed by spontaneous polymerization. $^{1-4}$ A reaction of styrene with compound 1 yields a copolymer by the free radical mechanism.⁴ Continuing our investigations, 1-4 we obtained the nearest higher homolog of compound 1, viz., 1-ethyl-1,2,2-trimethyl-1,2-disilacyclobutane (2), and studied its spontaneous polymerization and copolymerization with monomer 1.⁵ It turned out that such a configuration of substituents at the Si atoms (one ethyl and three methyl groups) makes compound 2 substantially less reactive in spontaneous room-temperature polymerization compared to tetramethyl derivative 1: the time required for complete conversion into the polymer increases from a few minutes to a week. To study the effect of the Me₃Si group at an endocyclic C atom on the reactivity of 1,2-DSCB in spontaneous polymerization as well as to estimate the asymmerty effect due to the presence of the Me_3Si group in the monomer unit on the properties of the resulting polymer, here we synthesized 1,1,2,2-tetramethyl-3-trimethylsilyl-1,2-disilacyclobutane (3) and examined its spontaneous polymerization.

Results and Discussion

Compound **3** was obtained in three steps (Scheme 1).

Scheme 1



The first two steps were implemented as described earlier.^{6,7} The last step presented few problems when the reac-

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tion conditions were similar to those used previously for the synthesis of compound 2. We found nearly optimum conditions for gas-phase dehalogenation of 1,2-bis[chloro-(dimethyl)silyl]-2-trimethylsilylethane (4) in a vacuum system.^{4,5} Slow supply of the vapor of compound 4 to a reaction tube is crucial for the success of this synthesis because a constant low pressure (0.1-0.5 Torr) and a constant temperature (270±5 °C) in the reaction zone are thus ensured. When these conditions are met, the dehalogenated product collected in cooled tubes is virtually individual compound 3 obtained in 45-52% yield. Strict observation of the above conditions for gas-phase dehalogenation is dictated by the fact that compound 3 cannot be purified by additional distillation (its boiling and melting points are substantially higher than those of disilacyclobutanes 1 and 2): even when flowing down into a cooled tube upon thawing, compound 3 already undergoes partial polymerization. Furthermore, this precluded us from recording its NMR spectrum. Sealed tubes with compound 3 were kept in liquid nitrogen before use. The mass spectrum of monomer 3 contains a considerable molecular ion peak with m/z 216 (33.5%), the most intense peak with m/z 201 (100%, $[M - Me]^+$), and intense peaks with m/z142 (89.5%), 141 (62.3%), and 127 (93.6%): [M – HSiMe₃]⁺, $[M - HSiMe_3 - H]^+$, and $[M - Me - HSiMe_3]^+$, respectively. The intensity of the peak with m/z 73 (Me₃Si) is 90.2%.

After warming of the tube with monomer **3** to room temperature, a noticeable exothermic process began. After ~40-45 min, immobile polymer **5** was obtained in 83-92% yield ($M_w = 3.47 \cdot 10^5 - 3.85 \cdot 10^5$, $M_w/M_n = 2.43 - 2.86$) (Scheme 2). Therefore, the presence of such a bulky group as Me₃Si at a carbon atom of the 1,2-DSCB ring decreases polymerization reactivity to a lesser extent than does the presence of a bulkier substituent at a silicon atom. As a result, the tendency of compound **3** toward spontaneous polymerization is much closer to that of compound **1** rather than **2**. This agrees with the fact that spontaneous polymerization of lower 1,2-DSCB homologs follows the freeradical mechanism involving cleavage of the Si-Si bond.

Polymer 5 is well soluble in common organic solvents. Its backbone consists of alternating dimethylsilylene ($Me_2Si-SiMe_2$) and trimethylsilylethylene units ($CH_2CHSiMe_3$); *i.e.*, it is formally an alternating copolymer of tetramethyldisilylene and trimethyl(vinyl)silane and an elastomer with the glass transition temperature $T_g = -8.9$ °C (DSC data). The amorphism of polymer 5 is obviously due to the structural asymmetry of monomer 3. Its polymerization produces a macromolecule containing blocks formed by two types of linkage between monomer units: "head-to-tail" (A) and "head-to-head" (B). This in turn ensures the diastereomerism of the units in the blocks, depending on whether two neighboring Me₃Si groups are on the same side or on opposite sides of the polymer backbone (see Scheme 2).

The structure of polymer **5** was determined by IR spectroscopy and ¹H, ¹³C, and ²⁹Si NMR spectroscopy. The IR spectrum shows intense bands at 1130 and 1017 cm⁻¹ (SiCHCH₂Si), a band at 1252 cm⁻¹ with a shoulder at 1258 cm⁻¹ and a band at 834 cm⁻¹ with a shoulder at 815 cm⁻¹ (SiMe₂ and SiMe₃), bands at 725 and 608 cm⁻¹ (Si—C bending vibrations), and very weak (though becoming pronounced upon magnification) bands at 433, 418, and 409 cm⁻¹ (Si—Si stretching vibrations).

Because each monomer unit in polymer 5 contains four types of protons (SiMe₃, SiMe₂, CH₂, and CH), we would expect four resonance lines in its ¹H NMR spectrum, with an integral intensity ratio of 9:12:2:1, respectively. In fact, the ¹H NMR spectrum of polymer 5 shows two intense signals at δ 0.20 and 0.28 (SiMe) and a signal at δ 1.01 (CH₂); the integral intensity ratio of the first two signals to the last one is 11:1. Obviously, the line due to the CH proton is masked by the intense signals for the protons of the SiMe groups.

The quantitative ¹³C NMR spectrum contains a group of lines at δ 9.04 (CH₂Si), a group of lines at δ 3.52 (CH), an intense signal at $\delta -0.13$ (Me₃Si), and five signals at δ 0.14, -1.52, -2.60, -2.72, and -3.65 (Me₂Si). This magnetic nonequivalence of the Me₂Si groups suggests that the backbone of polymer 5 consists of a random sequence of segments of different lengths that follow the "head-to-tail" (A) and "head-to-head" (B) linkage patterns (see Scheme 2). The presence of three silicon atoms in each monomer unit of polymer 5 is confirmed by its quantitative ²⁹Si NMR spectrum (short pulse (30%), a long relaxation delay, and proton decoupling) containing three lines of equal intensity at δ 2.97 (SiMe₃), -13.80, and -16.46 (SiMe₂). The spectra of polymer **5** exhibit no signals unique to the nuclei in either the block A or B, which precludes determination of a precise ratio of these blocks.





To sum up, like 1,1,2,2-tetramethyl- and 2-ethyl-1,1,2-trimethyl-1,2-disilacyclobutanes, 1,1,2,2-tetramethyl-3-trimethylsilyl-1,2-disilacyclobutane is highly reactive in spontaneous polymerization which involves ringopening cleavage of the Si—Si bond to give an amorphous high-molecular-weight polymer.

Experimental

¹H, ¹³C, and ²⁹Si NMR spectra were recorded on a Bruker DPX-400 spectrometer (400, 100.6, and 79.5 MHz, respectively) at 50–60 °C for saturated solutions of polymer **5** in deuterated toluene (C = 0.5–0.6 mol L⁻¹). Mass spectrum (EI) was measured on a Finnigan 4021 GC/MS instrument. IR spectra were recorded on Specord M-80 and SP-1200 instruments in the 400–3600 cm⁻¹ range. The molecular mass distribution of the polymer was determined by gel permeation chromatography on a Waters-200 instrument in toluene at 25 °C (flow rate 1.0 mL min⁻¹, three ultrastyragel columns with sorbent pore sizes of 100, 500, and 1000 Å). The instrument was calibrated against polystyrene standards. The glass transition temperature was measured on a Mettler TA-4000 differential scanning calorimeter with a DSC-30 heating cell (heating rate 20 deg min⁻¹, argon).

Freshly distilled toluene and ethanol were used for dissolution, precipitation, and washing of samples of the polymer.

1,1,2,2-Tetramethyl-3-trimethylsilyl-1,2-disilacyclobutane (3). Dehalogenation of compound 4 (pre-degassed in vacuo) with the alkali metal vapors was carried out in a flow vacuum system according to a known procedure.⁴ A tube with compound **4** was heated in such a way that its vapor was supplied to the reaction tube over a K/Na melt (270 °C, 0.1 Torr). The supply rate was regulated so that the reaction temperature was no higher than 275 °C and the pressure was no higher than 0.5 Torr. The dechlorination product (individual monomer 3) was collected in a flow trap cooled with liquid nitrogen. Careful heating of the trap allowed the monomer to flow down into calibrated tubes, which were sealed and kept in liquid nitrogen before use. In a typical experiment, the yield of individual disilacyclobutane 3 from dichloride 4 (4.62 g) was 1.62 g (48.7%). Found (%): C, 49.80; H, 10.95; Si, 39.23. C₉H₂₄Si₃. Calculated (%): C, 49.92; H, 11.17; Si, 38.91. MS (EI, 70 eV), m/z (I_{rel} (%)): 216/217/218 [M]⁺ $(33.5/7.8/3.9), 201/202/203 [M - Me]^+ (100/23.1/12.2),$ 173 (15.3), 145 (7.2), 144 (11.3), 143 [M - SiMe₃]⁺ (37.7), 142 $[M - HSiMe_3]^+$ (89.5), 141 $[M - HSiMe_3 - H]^+$ (62.3), 127 $[M - Me - HSiMe_3]^+$ (93.6), 115 (10.1), 85 (5.8), 73/74/75 [SiMe₃]⁺ (90.2), 59 (31.6), 45 (10.1), 43 (8.0).

Polymer 5. A sealed tube containing compound **3** (0.72 g, 3.3 mmol) was withdrawn from liquid nitrogen. Spontaneous,

highly exothermic polymerization began after thawing of the monomer at room temperature. The mobile liquid became thicker to give, in a period of 45 min, a clear rubbery mass. The tube was opened, and its contents was dissolved in toluene. Polymer 5 was precipitated with ethanol. The resulting precipitate was dissolved again, reprecipitated, washed with ethanol, and dried in a vacuum desiccator at 50 °C to a constant weight. Yield 0.64 g (89%). Found (%): C, 50.11; H, 10.98; Si, 39.17. (C₉H₂₄Si₃)_x. Calculated (%): C, 49.92; H, 11.17; Si, 38.91. ¹H NMR (CD₃C₆D₅), $\delta:~0.20$ and 0.28 (both w, $SiMe_3,~SiMe_2,$ and SiCHSi); 1.01 (w, CH₂). ¹³C NMR (CD₃C₆D₅), δ : -3.65, -2.72, -2.60, -1.52, 0.14 (Me₂Si); -0.13 (SiMe₃); 3.52 (CH); 9.04 (CH₂). ²⁹Si NMR $(CD_3C_6D_5)$, δ : -16.46 (SiMe₂); -13.80 (SiMe₂); 2.97 (SiMe₃). IR, v/cm⁻¹: 2936 (v^{as}(Me)); 2883 (sh 2854) (v^{as}CH₂; v^sMe); 2808 (v^sCH₂); 1252 (sh 1258) (δ^sMeSi); 1190; 1130, 1017 (SiCH₂CHSi); 965; 936; 858; 834 (sh 815) (SiMe₂ and SiMe₃); 780; 740; 725 (δ (Si-C)); 699; 680; 660; 644; 608 (δ (Si-C)); 570; 433, 418, 409 (v(Si-Si)).

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