2524 *Macromolecules* **1997,** *30,* 2524−2526

Anionic Polymerization of 3-Methylenesilacyclobutanes and Reactivity of Poly(3-methylenesilabutane)s

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Received December 18, 1996

Revised Manuscript Received February 24, 1997

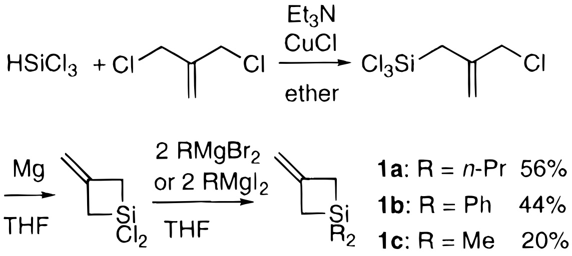
Introduction. Silacyclobutane is one of the most important monomers to synthesize poly(carbosilane)s. Many workers have studied the polymerization of silacyclobutane derivatives for the last three decades.[1] Among numerous kinds of silacyclobutane derivatives, 3-methylenesilacyclobutanes are particularly interesting because they have not only a four-membered strained ring but also diallylmetal structures. Damrauer and coworkers reported the synthesis of 1,1-dichloro-3-methylenesilacyclobutane in 1990,[2] and Utimoto et al. studied the reactivities of 1,1-dipropyl- and 1,1-diphenyl-3-methylenesilacyclobutanes.[3] We decided to investigate polymerization of 3-methylenesilacyclobutanes. Poly(3-methylenesilabutane)s, which can be obtained from ring-opening polymerization of the monomers, are a new series of reactive polymers because they consist of an allylsilane repeat unit having C═C bonds exo to the polymer main chain. We describe here anionic polymerization of 3-methylenesilacyclobutanes and reactivities of the polymers.

Results and Discussion. Three different kinds of 3-methylenesilacyclobutane derivatives, namely, 1,1-dimethyl-3-methylenesilacyclobutane (**1c**), 3-methylene-1,1-dipropylsilacyclobutane (**1a**), and 3-methylene-1,1-diphenylsilacyclobutane (**1b**), were synthesized. These monomers were obtained by the reactions shown in Scheme 1.[3]

Anionic polymerization of 3-methylenesilacyclobutane (Scheme 2) was carried out under an argon atmosphere. Butyllithium was used as an initiator, and methanol was used as a terminator.[4] Table 1 summarizes the results. Addition of 5 mol % of butyllithium to a THF solution of **1a** at −78 °C gave poly(3-methylene-1,1-dipropylsilabutane) (**2a**) in 98% yield ($M_n = 6400$, $M_w/M_n = 1.76$, determined by GPC using polystyrene as a standard). Similarly, addition of 2 mol % of butyllithium to a THF solution of **1a** provided polymer **2a** ($M_n = 28\,000$, $M_w/M_n = 2.21$). When **1b** or **1c** was polymerized by addition of 2 mol % of butyllithium, poly(3-methylene-1,1-diphenylsilabutane) (**2b**) ($M_n = 15\,000$, $M_w/M_n = 2.25$) or poly(1,1-dimethyl-3-methylenesilabutane) (**2c**) ($M_n = 6900$, $M_w/M_n = 2.88$) was obtained.

Monomer **1a** was polymerized under other conditions but did not give satisfactory results. Although polymerization took place readily in the presence of hexamethylphosphoramide (HMPA),[5] isomerization of the C═C occurred[6] and polymer **2a** could not be obtained selectively. When benzene or hexane was used for the solvent, polymerization did not take place even at room temperature.[7]

Scheme 1



Scheme 2

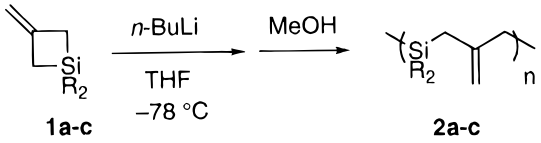
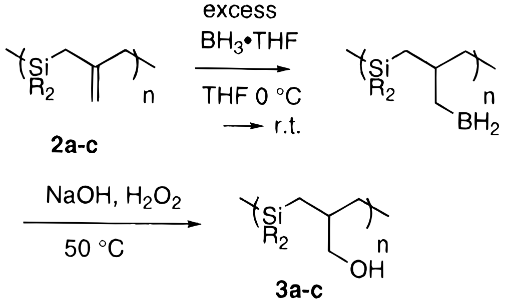


Table 1. Polymerization of 3-Methylenesilacyclobutanes

run	monomer	$[M]_0/[I]_0$[a]	M_n[b]	M_w/M_n[b]
1	**1a** (R = *n*-Pr)	20	6400	1.76
2	**1a** (R = *n*-Pr)	50	28000	2.21
3	**1b** (R = Ph)	20	5500	2.20
4	**1b** (R = Ph)	50	15000	2.25
5	**1c** (R = Me)	20	5800	2.88

[a] Ratio of the initial concentration of the monomer and initiator. [b] Determined by GPC relative to standard polystyrene.

Scheme 3



Although allylorganosilanes are usually stable toward oxygen, the polymers prepared above were not. The instability of the polymer in oxygen was confirmed by the following experiment. Dry oxygen was introduced to a THF solution of polymer **2a**. After 18 and 48 h, a portion of the solution was taken out and the molecular weight of the resulting mixture was measured by GPC. Decomposition of the polymer was clearly indicated by the decrease of the molecular weight of the polymer.[8] To obtain more information about the decomposed product, an IR spectrum of the resulting mixture was taken and exhibited a broad absorption at 3400 cm^{-1}. This band suggests the presence of hydroxy groups.[9] The proton NMR spectrum of the decomposed product was also taken, but no apparent difference from that of the starting material was detected.

To explore the poly(3-methylenesilabutane)s as reactive polymers, a hydroboration reaction[10] was examined. Treatment of **2a** with BH_3·THF in THF followed by the H_2O_2−NaOH oxidation gave poly(3-(hydroxymethyl)-1,1-dipropylsilabutane) (**3a**) (Scheme 3).[11] The complete transformation of the methylene groups into hydroxymethyl groups was confirmed by the ^{1}H NMR spectrum of polymer **3a**. The diphenyl-substituted polymer **2b** or dimethyl-substituted polymer **2c** could also be transformed into the corresponding poly(3-(hydroxymethyl)-silabutane) **3b** or **3c**, respectively. The solubilities of the polymers were measured. Polymer **3a** was soluble both in nonpolar solvents such as toluene or chloroform and in polar solvents such as dimethyl sulfoxide (DMSO) or ethanol. Polymer **3b** was soluble in DMSO but insoluble in toluene, chloroform, and ethanol. Polymer **3c** was soluble in polar solvents such as DMSO, ethanol,

S0024-9297(96)01865-7 CCC: $14.00

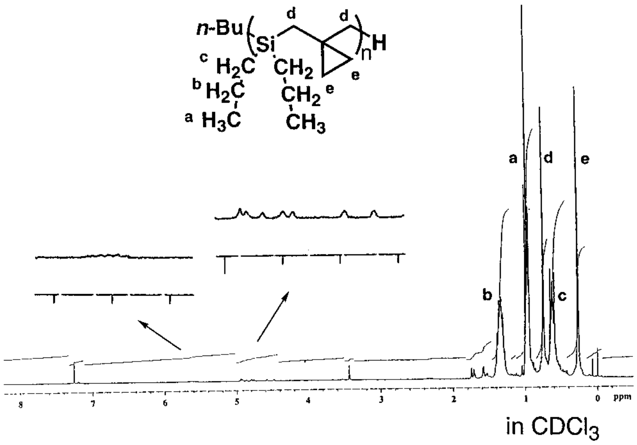
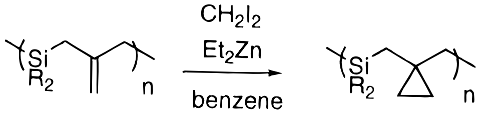


Figure 1. ^{1}H NMR spectrum of poly(3-(cyclopropyl)-1,1-dipropylsilabutane) (**4a**).

Scheme 4



2a **4a**

and methanol but insoluble in nonpolar solvents such as toluene or chloroform.

Cyclopropanation[12] of the C=C was examined. Addition of diethylzinc to a mixture of polymer **2a** and diiodomethane in benzene provided polysilabutane **4a**, which has a cyclopropane ring in the main chain (Scheme 4).[13]

In contrast to hydroboration, however, cyclopropanation was accompanied with side reactions. Figure 1 shows the ^{1}H NMR spectrum of the reaction product. Small signals at δ 4.45 and 4.58 ppm were observed and were assigned to isopropenyl methylene protons. It is assumed that a backbone cleavage reaction occurred which afforded isopropenyl groups. This is consistent with the fact that M_n of the polymer decreased from 6600 to 4500 during the cyclopropanation. Other small signals at 4.72–4.78 and 5.60 ppm are ascribed to olefin protons in the vinyl group that might be formed by a thermal ring-opening reaction of cyclopropane.[14]

In summary, 3-methylenesilacyclobutanes can be readily polymerized by using butyllithium as an initiator, and poly(3-methylenesilabutane)s were useful as reactive polymer intermediates. Other polymer reactions of 3-methylenesilabutanes are under investigation.

Acknowledgment. The present work was supported by Grants-in-aid for Scientific Research Nos. 08246228 and 08751026 from the Ministry of Education, Science, Sports, and Culture, Japan. We thank Professor Kiitiro Utimoto of Kyoto University for his assistance with NMR measurement.

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(2) Damrauer, R.; Simon, R.; Laporteie, A.; Manuel, G.; Park, Y. T.; Weber, W. P. *J. Organomet. Chem.* **1990**, *391*, 7.

(3) Okada, K.; Matsumoto, K.; Oshima, K.; Utimoto, K. *Tetrahedron Lett.* **1995**, *36*, 8067.

(4) A typical polymerization procedure was as follows. Into a 100-mL round-bottomed flask, equipped with a Teflon-covered magnetic stirring bar, rubber balloon, and rubber septum were placed 3-methylene-1,1-dipropylsilacyclobutane (**1a**; 814 mg, 4.84 mmol) and THF (10 mL) under an argon atmosphere. The mixture was cooled to −78 °C, and a hexane solution of butyllithium (1.61 M, 0.15 mL, 0.242 mmol) was added via a syringe. The reaction mixture was stirred at −78 °C for 30 min, and methanol (0.5 mL) was added. After being stirred for 5 min, the resulting mixture was poured into water and extracted with toluene (50 mL). The organic layer was separated and dried over anhydrous sodium sulfate. The volatile solvents were removed under reduced pressure to give poly(3-methylene-1,1-dipropylsilabutane) (**2a**, 795 mg) in 98% yield. IR (neat): 2950, 2922, 2866, 1621, 1456, 1409, 1374, 1332, 1277, 1204, 1158, 1066, 1031, 854 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 0.48–0.75 (m, 4H), 0.97 (t, J = 7.0 Hz, 6H), 1.23–1.50 (m, 4H), 1.50 (s, 4H), 4.43 (s, 2H). ^{13}C NMR (CDCl$_3$): δ 15.31, 17.32, 18.53, 24.77, 106.31, 144.87. $M_n = 6400$, $M_w/M_n = 1.76$ (determined by GPC using polystyrene as a standard).

(5) Anionic polymerization of 1,1-dimethylsilacyclobutene in THF in the presence of HMPA was reported in ref 1j.

(6) The ^{1}H NMR spectrum of poly(1,1-dimethyl-3-methylenesilabutane) prepared in the presence of HMPA showed small signals at 4.45 and 1.64 ppm, which can be assigned to olefin methyne proton and allylic methyl protons.

(7) Addition of butyllithium to **2a** in benzene or hexane at room temperature gave only butyl(2-methyl-2-propenyl)dipropylsilane, and no polymeric product was obtained. Nucleophilic attack on the monomer by a propagating allylic anion did not take place under these conditions.

(8) The weight average molecular weight of the polymer decreased from 20 000 (0 h) to 10 000 at 18 h and then 2300 at 45 h.

(9) It is assumed that the decomposition pathway is as follows. Oxidation of the C=C bond gave epoxidated compound, which was hydrolyzed into allylic alcohol and silanol.

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(11) A typical hydroboration–oxidation procedure of the polymer was as follows. Borane–tetrahydrofuran complex (1.0 M THF solution, 1.79 mL, 1.79 mmol) was added to a solution of **2a** ($M_n = 2900$, $M_w/M_n = 2.60$, 301 mg) in THF (3.6 mL) at 0 °C under an argon atmosphere. After being stirred for 30 min, the mixture was warmed to room temperature and stirred for 1 h. An aqueous sodium hydroxide (3 M, 1.79 mL) and 30% aqueous H_2O_2 solution were added to the mixture and stirred for an additional 2 h. The resulting mixture was poured into excess hexane to precipitate the polymer, which was dried under vacuum. In this way, poly(3-(hydroxymethyl)-1,1-dipropylsilabutane) (**3a**, 333 mg) was obtained in quantitative yield. IR (neat): 3278 (broad), 2950, 2918, 1460, 1411, 1374, 1332, 1201, 1064, 1003, 893, 855 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 0.30–1.00 (m, 8H), 0.95 (t, J = 7.0 Hz, 6H), 1.22–1.42 (m, 4H), 1.72–1.88 (m, 1H), 3.23–3.58 (m, 2H), 4.20–5.30 (broad, 1H). ^{13}C NMR (CDCl$_3$): δ 16.66, 17.46, 19.10, 19.69, 33.67, 69.26. $M_n = 3200$, $M_w/M_n = 2.63$ (determined by GPC using polystyrene as a standard).

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(13) The cyclopropanation procedure was as follows. Diethylzinc (1.0 M hexane solution, 4.34 mL, 4.34 mmol) was added to a mixture of **1a** ($M_n = 6600$, $M_w/M_n = 2.97$, 609 mg) and diiodomethane (0.437 mL, 5.43 mmol) in benzene (3.6 mL) at room temperature under an argon atmosphere. After being stirred for 4 h, the reaction mixture was poured into 1 M HCl, extracted with toluene, and dried over anhydrous

Na_2SO_4. The volatile solvents were removed under reduced pressure to give poly(3-(cyclopropyl)-1,1-dipropylsilabutane) (**4a**, 651 mg) in quantitative yield. IR (neat): 2950, 2922, 2866, 1458, 1410, 1374, 1332, 1283, 1203, 1066, 1010, 874, 810, 753 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.27 (s, 4H), 0.40−78 (m, 4H), 0.74 (s, 4H), 0.94 (t, J = 7.2 Hz, 6H), 1.22−1.44 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 14.53, 15.69, 17.65, 17.94, 18.74, 25.28. $M_n = 4500$, $M_w/M_n = 2.99$ (determined by GPC using polystyrene as a standard).

(14) This mechanism was confirmed by the fact that heating **3a** at 180 °C for 6 h under argon gave 37% cyclopropane-ring-opened polymer.

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