Macromolecules **1995,** *28,* 7029−7031

Living Anionic Ring-Opening Polymerization of 1,1-Dimethylsilacyclobutane

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Received June 1, 1995
Revised Manuscript Received July 25, 1995

Introduction. Polycarbosilanes have recently attracted much attention because of their unique characteristics compared to the usual hydrocarbon polymers.[1,2] The development of synthetic methods to obtain well-defined polycarbosilanes is indispensable for the detailed investigations of the chemical and physical properties of polycarbosilanes and their application to functional materials.

Among many kinds of polycarbosilanes, polysiltrimethylenes are fundamental. They can be readily prepared from silacyclobutanes,[3] which are easily accessible or commercially available. They have relatively high reactivities due to ring strain. Although considerable work has been done on the anionic,[4] thermal,[5] and transition-metal-catalyzed[6] ring-opening polymerization of 1,1-dimethylsilacyclobutane (**1**), no study has been reported on the synthesis of poly(1,1-dimethylsilabutane) with well-controlled molecular weight and sufficiently narrow molecular weight distribution. In this paper, we describe anionic polymerization of 1,1-dimethylsilacyclobutane proceeding with a living nature (Scheme 1).

Results and Discussion. Liao and Weber recently reported that butyllithium induced polymerization of silacyclobutane derivatives such as 1,1-divinylsilacyclobutane,[7] 1,1-dihydridosilacyclobutane,[8] and 1,1-dimethylsilacyclobutene[9] in THF at −78 °C in the presence of HMPA. An attempt to apply the same conditions for a polymerization of 1,1-dimethylsilacyclobutane (**1**) resulted in a formation of poly(1,1-dimethylsilabutane) with broad molecular weight distribution (MWD) (M_w/M_n = 1.63, estimated by GPC, polystyrene as a standard). Then we examined butyllithium-induced polymerization of **1** in the absence of HMPA. Table 1 summarizes the results.

The polymerization in THF at −78 °C was incomplete, and the polymer was obtained in only 62% yield even after the prolonged reaction time (run 1). In contrast, polymerization of **1** in THF at −48 °C gave poly(1,1-dimethylsilabutane) quantitatively with a narrow MWD (M_w/M_n = 1.12) (run 2). Polymerization at higher temperature (0 °C) provided a polymer with a broader MWD (M_w/M_n = 1.47) (run 3). Polymerization in diethyl ether at 0 °C also gave a polymer with a broad MWD (M_w/M_n = 1.42) (run 5). Although polymerization in run 2 readily proceeded to give polymer with narrow MWD, it did not show a living nature. This is confirmed by the following results. The addition of 2 mol % of butyllithium to a solution of monomer **1** in THF at −48 °C provided the polymer in only 91% yield (run 6). An addition of fresh feed of monomer **1** to the polymerization mixture did not restart polymerization, and neither the yield nor the number-average molecular weight (M_n) of the polymer increased (run 7). We assumed that the polymerization in THF at −48 °C did not have the living nature because of the low solubility of the produced polymer in THF. In fact, a white precipitate appeared several minutes after the addition of butyllithium to the monomer.

Scheme 1

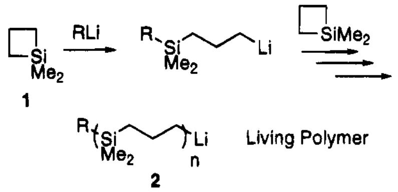

Table 1. Polymerization of 1,1-Dimethylsilacyclobutane in THF or Ether[a]

run	**1** (mmol)	*n*-BuLi (mmol)	solvent	temp (°C)	yield (%)	M_n[b]	M_w/M_n[c]
1	5.0	0.25	THF	−78	62	1700	
2	5.0	0.25	THF	−48	100	2400	1.12
3	5.0	0.25	THF	0	100	4400	1.47
4	5.0	0.25	ether	−48	0		
5	5.0	0.25	ether	0	95	2700	1.42
6	10.0	0.20	THF	−48	91	6400	1.23
7	5.0 + 5.0[d]	0.25	THF	−48	114	3100	1.25

[a] Polymerization was carried out in a solvent (10 mL in runs 1−5 and 7 and 20 mL in run 6). The reaction time was 4 h (run 1) or 1 h (runs 2−7). [b] Determined by ^{1}H NMR (from the integral ratio of termination end methyl group absorption at δ 0.94 to methylene group absorption at δ 0.52−0.59). [c] Estimated by GPC (polystyrene standard). [d] The equal amount of monomer was added in two portions. The second portion was added to the reaction mixture 20 min after the initiation of the polymerization.

Scheme 2

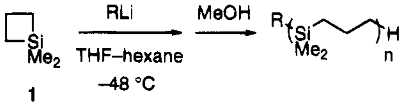

Table 2. Polymerization of 1,1-Dimethylsilacyclobutane in THF−Hexane[a]

run	solvent	initiator	**1** (mmol)	initiator (mmol)	yield (%)	M_n[b]	M_w/M_n[c]
1	THF−hexane	*n*-BuLi	5.0	0.25	99	2400	1.10
2	THF−hexane	*n*-BuLi	10.0	0.20	98	5100	1.14
3	THF−hexane	*n*-BuLi	5.0 + 5.0[d]	0.25	200	4600	1.17
4	THF−hexane	PhLi	5.0	0.25	100	2500	1.17
5	THF−hexane	PhLi	10.0	0.20	97	6100	1.26

[a] Polymerization was carried out in THF (5 mL)−hexane (5 mL) in runs 1, 3, and 4 and in THF (10 mL)−hexane (10 mL) in runs 2 and 5 at −48 °C. [b] Determined by ^{1}H NMR (from the integral ratio of termination end methyl group absorption at δ 0.94 to methylene group absorption at δ 0.52−0.59). [c] Estimated by GPC (polystyrene standard). [d] The equal amount of monomer was added in two portions. The second portion was added to the reaction mixture 20 min after the initiation of the polymerization.

To solve this problem, we examined the polymerization in various solvents and found that THF−hexane mixed solvent was satisfactory (Scheme 2). Table 2 shows the results. Addition of 5 mol % of butyllithium to a solution of 1,1-dimethylsilacyclobutane in THF−hexane (1:1) at −48 °C afforded almost monodispersed poly(1,1-dimethylsilabutane) (M_w/M_n = 1.10) in 99% yield (run 1).[10]

The time−yield curve for the butyllithium-induced polymerization of 1,1-dimethylsilacyclobutane in THF−hexane at −48 °C was shown in Figure 1. Polymerization proceeded readily without an induction period and was complete within 20 min after the addition of butyllithium. The relationship between M_n and yield of the polymer is shown in Figure 2. M_n increased in proportion as the yield of polymer increased, although the increase of the M_n is greater to some extent than that calculated from a rate of the amount of the

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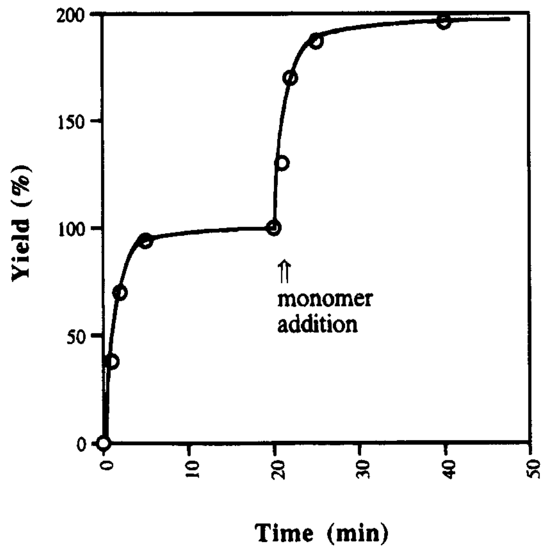


Figure 1. Time–yield curve for the butyllithium-induced polymerization of **1** in THF (5 mL) and hexane (5 mL) at −48 °C: **1** (5.0 mmol), *n*-BuLi (0.25 mmol). 5.0 mmol of **1** was added at 20 min.

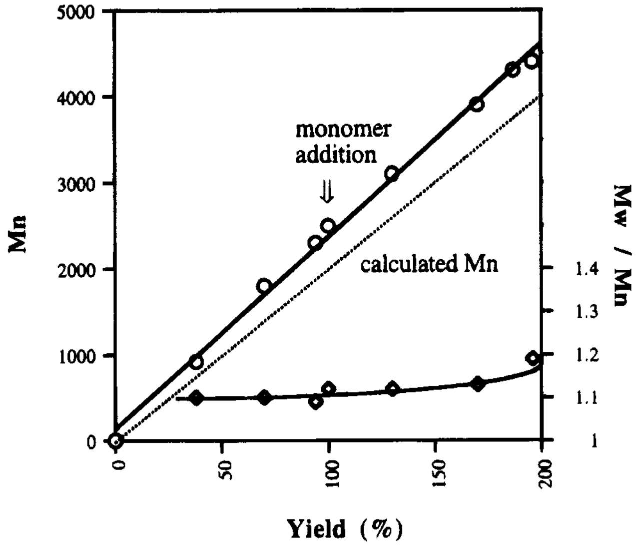
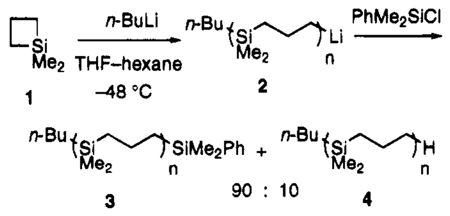


Figure 2. M_n curve and M_w/M_n curve for the buthyllithium-induced polymerization of **1**: **1** (5.0 mmol), *n*-BuLi (0.25 mmol) in THF (5 mL) and hexane (5 mL) at −48 °C. 5.0 mmol of **1** was added at 20 min.

Scheme 3



converted monomer and initiator. Under these reaction conditions, higher molecular weight polymer could be obtained quantitatively. For example, treatment of the monomer **1** with 2 mol % of butyllithium in THF–hexane at −48 °C gave poly(1,1-dimethylsilabutane) in 98% yield (run 2).

To investigate the living nature of this polymerization, the second fresh feed of the monomer **1** was introduced to the reaction mixture after the initial charge of the monomer had been polymerized. The added 1,1-dimethylsilacyclobutane smoothly polymerized at the same rate as in the initial stage, and both the yield and the M_n of the polymer increased (Figures 1 and 2 and Table 2, run 3). Figure 2 also shows the M_w/M_n curve for the polymerization. The molecular weight dispersity was kept narrow ($M_w/M_n < 1.19$) even after the second addition of the monomer. Phenyllithium instead of butyllithium also induced the polymerization of 1,1-dimethylsilacyclobutane, but the phenyllithium-induced polymerization proceeded with a broader MWD than that of butyllithium-induced polymerization (runs 4 and 5).

We also examined the end capping of the resulting polymer with an electrophile. Treatment of the polymer prepared from 1,1-dimethylsilacyclobutane and 5 mol % of butyllithium in THF–hexane at −48 °C with chlorodimethylphenylsilane provided dimethylphenylsilylated polymer **3** (Scheme 3).[11] The end-capping efficiency (**3**/(**3** + **4**)) was 0.90.

On the basis of these results, we are tempted to assume that the polymerization of **1** has proceeded in a living manner and living polymer **2** has been produced during the whole polymerization process.

Acknowledgment. The present work was supported by Monbusho International Scientific Research Program: Joint Research No. 06044114. We thank Professor M. Sawamoto for useful discussions. We are also grateful to Professors K. Utimoto and K. Oshima for their assistance with the NMR measurement.

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(10) The experimental procedure was as follows. In a 100-mL round-bottomed flask, equipped with a Teflon-covered magnetic stirring bar, rubber balloon, and rubber septum, were placed 1,1-dimethylsilacyclobutane (**1**; 0.646 mL, 5.0 mmol), THF (5 mL), and hexane (5 mL) under an argon atmosphere. The mixture was cooled to −48 °C, and a hexane solution of butyllithium (1.62 M, 0.154 mL, 0.25 mmol) was added via syringe. The reaction mixture was stirred at −48 °C for 1 h, and then methanol (1.0 mL) was added. After being stirred for 5 min, the resulting mixture was poured into brine and extracted with toluene (50 mL). The organic layer was separated, washed with water (30 mL), and dried over anhydrous sodium sulfate. The volatile solvents were removed under reduced pressure to give poly(1,1-dimethylsilabutane) (512 mg) in 99% yield. ^{1}H NMR ($CDCl_3$): δ

−0.07 (s, 138H), 0.52−0.59 (m, 92H), 0.87 (t, *J* = 6.9 Hz, 3H), 0.94 (t, *J* = 7.1 Hz, 3H), 1.20−1.38 (m, 50H).

(11) Butyllithium (1.62 M, 0.154 mL, 0.25 mmol) was added to a solution of **1** (0.646 mL, 5.0 mmol) in THF (5 mL) and hexane (5 mL) at −48 °C. The reaction mixture was stirred for 20 min, and then chlorodimethylphenylsilane (0.33 mL, 2.0 mmol) was added. After being stirred for 30 min, methanol (1.0 mL) was added. The resulting mixture was poured into brine and extracted with toluene. The organic layer was separated and dried over anhydrous sodium sulfate. Some amount of toluene was evaporated. The polymer solution was poured into methanol, reprecipitated twice from toluene into methanol, and dried *in vacuo* to give polymers **3** and **4** in 92% yield. The end-capping efficiency was determined by ^{1}H NMR (from the integral ratio of the termination end phenyl group absorption at δ 7.31−7.37 and δ 7.46−7.54 to the initiation end methyl group absorption at δ 0.87).

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