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Synthesis of Poly(1,3-adamantane)s by Cationic Ring-Opening Polymerization of 1,3-Dehydroadamantanes

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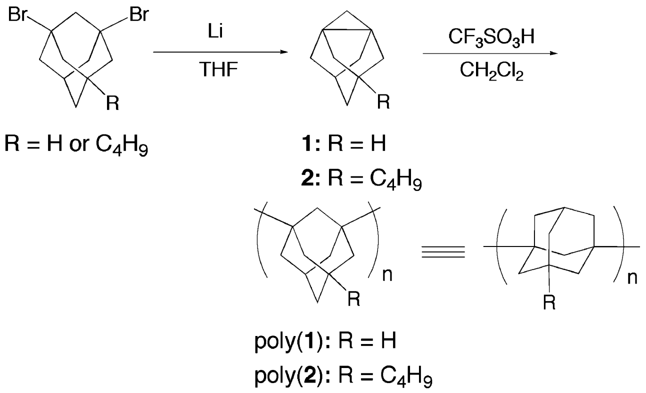
Small ring propellanes such as [1.1.1]-,[1] [2.2.2]-,[2] and [2.2.1]propellanes[3] have been of considerable interest because of the high reactivity derived from inverted tetrahedral geometry at the bridgehead carbons.[4,5] In the field of polymer chemistry, these highly strained propellanes can be positioned as cyclic monomers because of their ring-opening polymerizability. In fact, several oligomers and polymers have been obtained only via the ring-opening polymerizations of [1.1.1]propellane derivatives.[6−9]

1,3-Dehydroadmantane (**1**)[10,11] is a typical [3.3.1]-propellane derivative[12] and involves a tricyclic system fused by three methylene rings. An inverted 1,3 carbon−carbon bond of **1** readily undergoes free-radical and electrophilic ring-opening reactions with oxygen, bromine, and acetic acid to produce 1,3-disubstituted adamantanes. Interestingly, Pincock has reported that an insoluble polymeric product is formed by heating of this strained hydrocarbon at 130−160 °C.[10] Although the resulting product is supposed to be a poly(1,3-adamantane) only by IR spectroscopy and elemental analysis, the poor solubility has precluded its detailed characterization such as NMR spectroscopy, size exclusion chromatography (SEC), and viscosity measurement. To the best of our knowledge, no systematic studies on the ring-opening polymerization of 1,3-dehydroadamantanes and the synthesis of poly(1,3-adamantane)[13] have been reported.[14] Therefore, we have purposefully designed a novel 5-butyl-1,3-dehydroadamantane, **2**, by introducing a flexible butyl substituent on the adamantane skeleton in order to increase the solubility of the resulting polymer.[15] In this communication, we report the first synthesis of soluble poly(1,3-adamantane) via the cationic ring-opening polymerization of **2**.

The 1,3-dehydroadamantanes, **1** and **2**,[16] were synthesized by the reaction of 1,3-dibromoadamantane or 5-butyl-1,3-dibromoadamantane with lithium in THF at room temperature in 71 and 83% yields (Scheme 1), respectively. The monomers were purified by vacuum distillation to remove ethers and were alternatively diluted with CH_2Cl_2. The resulting 1,3-dehydroadamantanes were very stable in a sealed tube in C_6D_6 at least for several months, and no degradation and oligomerization were observed. However, they spontaneously reacted with oxygen to give the copolymeric products, as previously reported.[10] Therefore, we carefully treated with **1** and **2** in an all-glass apparatus under high-vacuum conditions.

Scheme 1



At first, when **1** was reacted with CF_3SO_3H in CH_2Cl_2 at 0 °C for 6 h (Table 1, run 1), some white precipitate was observed in the reaction mixture. Although a polymeric product was obtained in 95% yield after quenching with acetic acid,[17] it was insoluble in any organic solvents as previously reported.[10,18] Although we have thus found that the cationic polymerization of **1** also provides the poly(**1**) as well as the thermal polymerization,[19] its poor solubility prohibits further characterization.

We then attempted to cationically polymerize a novel butyl-substituted monomer **2** with CF_3SO_3H in CH_2Cl_2 at 0 °C for 6 h. A white precipitate similarly formed within several minutes, and the polymerization of **2** proceeded in the heterogeneous system. A polymer of white powder was obtained by precipitation into methanol in good yield after termination.[17] In contrast to the poor solubility of poly(**1**), the obtained polymer was soluble in several organic solvents such as chloroform, THF, and 1,2-dichlorobenzene[20] but insoluble in hexane, benzene, methanol, and water. The chemical structure of the resulting polymer was thoroughly characterized by ^1H and ^{13}C NMR spectroscopies in conjunction with IR measurement and elemental analysis.[21] Both ^1H and ^{13}C NMR spectra of the polymer showed all the signals expected to the repeating unit of poly(5-butyl-1,3-adamantane), poly(**2**). In the ^{13}C NMR spectra of 1-butyladamantane and **2**, 8 and 11 signals expected on the basis of their molecular symmetries are respectively observed, as shown in Figure 1. The signals of adamantane skeletons of **2** split and drastically shift from those of 1-butyladamantane toward the downfield region, except for one methylene carbon away from the propellane bond. After the polymerization, 11 reasonable signals are also detected, while one of the adamantyl methylene carbon and quaternary carbon substituted with a butyl group are overlapped at 34.0 ppm. Most of the signals corresponding to the adamantane skeleton again moved to the upfield region, where the signals of 1-butyladamantane are located, suggesting the drastic change of electronic environment.[22] Most importantly, the characteristic signal of inverted quaternary carbon of **2** at 36.1 ppm completely disappears, and alternatively a new signal corresponding to the internal quaternary carbon of main chain linkage appears at 38.5 ppm after the polymerization. These results strongly indicate that the ring-opening polymerization of **2** exclusively occurs to give a poly(5-butyl-1,3-adaman-

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Table 1. Cationic Polymerization of 1 and 2 in CH_2Cl_2 at 0 °C[a]

run	monomer type, mmol	CF_3SO_3H, mmol	M/I[b]	time, h	yield,[c] %	$10^{-3}M_n$(SEC)[d]	M_w/M_n[d]	T_{10},[e] °C
1	**1**, 3.39	0.41	8.3	6	95[f]	*g*	*g*	421
2	**2**, 2.85	0.52	5.5	6	89	1.5	1.30	445
3	**2**, 7.70	0.36	21	6	78	3.2	1.43	472
4	**2**, 8.66	0.19	46	6	52	4.4	1.56	485
5	**2**, 8.66	0.19	46	42	72	6.0	1.56	486

[a] Carried out under high-vacuum conditions (10^{-6} mmHg). [b] Initial molar ratio between monomer to initiator. [c] Methanol-insoluble part. [d] Estimated SEC measurement calibrated by polystyrene standards in 1,2-dichlorobenzene at 135 °C. [e] 10% weight loss temperature measured by TGA under nitrogen. [f] $CHCl_3$-insoluble part. [g] No data due to the poor solubility.

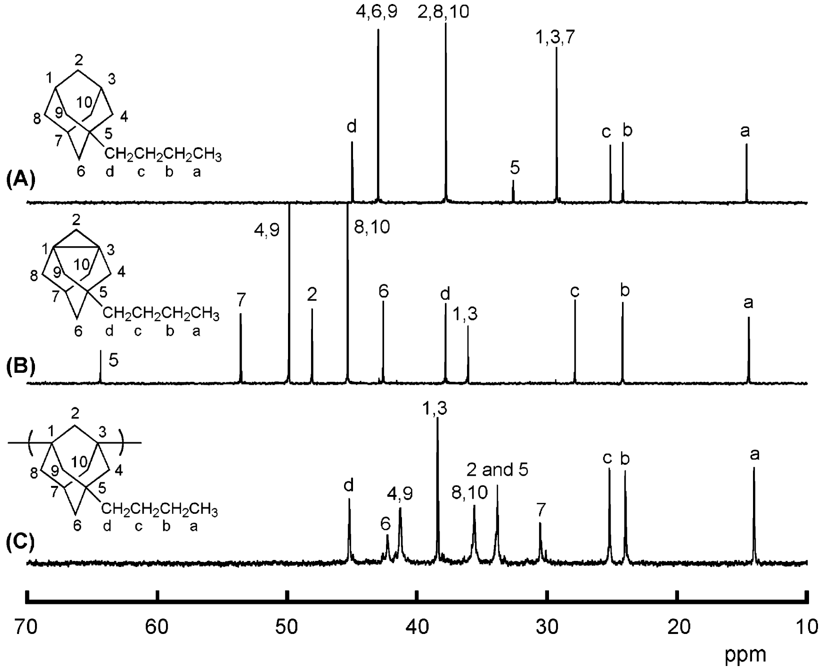

Figure 1. ^{13}C NMR spectra of 1-butyladamantane in $CDCl_3$ (A), **2** in C_6D_6 (B), and poly(**2**) in 1,2-dichlorobenzene/C_6D_6 (10/1) (C).

tane) through breaking of the 1,3-propellane σ-bond. Furthermore, this also supports the similar chemical structure of poly(**1**) containing an adamantane-1.3-diyl linkage via the ring-opening polymerization of **1**.

Table 1 shows the polymerization result of **2**. When the polymerizations were performed at the low monomer-to-initiator ratios (M/I) (runs 2 and 3), the polymer yields reached 80−90% within 6 h at 0 °C. At higher feed ratio of M/I = 46, the polymerization of **2** slowly proceeded and gave poly(**2**) in 52% yield after 6 h. Under similar conditions, the polymer yield increased to 72% after 42 h polymerization (run 5). The SEC curves of poly(**2**) measured in 1,2-dichlorobenzene were always unimodal, and the polydispersity indices, M_w/M_n, were 1.3−1.6. The SEC curves shift toward higher molecular weight side as the M/I ratios increase from 6 to 21, and 46, as shown in Figure 2. The M_n value estimated by using polystyrene standards reached 6000 at 72% yield[23] when the polymerization was carried out at 0 °C for 42 h. The number-average degree of polymerization of this poly(**2**) sample could be estimated at greater than 30. The molecular weights of poly(**2**) can be controlled to some extent by changing the feed molar ratio of monomer to initiator, indicating the infrequent chain transfer and termination reactions. This means that a propagating 1-adamantyl triflate[24] at the bridgehead position is fairly stable during the course of cationic ring-opening polymerization of **2**. This is supported by the unusual stability of the nonplanar 1-adamantyl carbocation due to the hyperconjugation effect through the rigid adamantane skeleton, as previously pointed out.[25−27] In addition, 1,2-elimination of the 1-adamantyl cation is strongly prevented because the resulting alkene, adamantene, is highly distorted,[28−30] if produced.

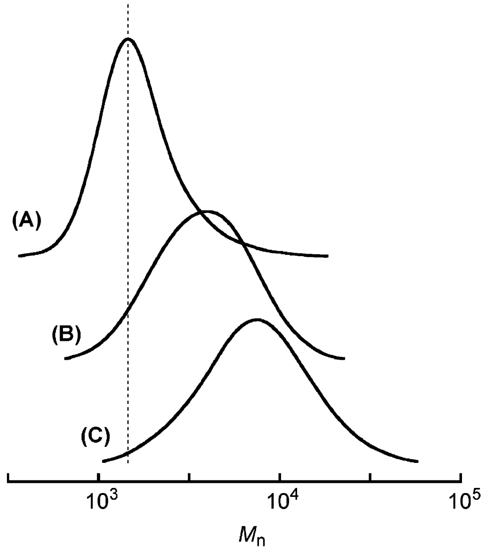

Figure 2. SEC curves of poly(**2**)s measured in 1,2-dichlorobenzene at 135 °C. Peak A: run 2, M/I = 5.5, M_n = 1500, M_w/M_n = 1.30. Peak B: run 3, M/I = 21, M_n = 3200, M_w/M_n = 1.43. Peak C: run 5, M/I = 46, M_n = 6000, M_w/M_n = 1.56.

The TGA analysis of poly(**1**) and poly(**2**) showed 10% weight loss at 421 and 486 °C under nitrogen, respectively. It is certain that this high thermal stability of both aliphatic polymers derives from the strain-free adamantane skeletons and the stable carbon−carbon bond between two bulky adamantane rings.

In conclusion, we have successfully synthesized a new all-hydrocarbon poly(propellane), poly(5-butyl-1,3-adamantane), showing good solubility and thermal stability via the cationic ring-opening polymerization of 5-butyl-1,3-dehydroadamantane. A detailed investigation on the polymerizability and the polymerization behavior of 1,3-dehydroadamantanes is now in progress.

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(13) The framework of poly(1,3-adamantane)s can be involved in the diamond lattice, as previously shown in ref 14.

(14) Reinhardt, H. F. *Polym. Lett.* **1964**, *2*, 567. Through another synthetic route, insoluble poly(1,3-adamantane) was similarly obtained by the Wurtz-type coupling reaction of 3,3′-dibromo-1,1′-biadamantane with sodium in xylene.

(15) Ishizone, T.; Tajima, H.; Matsuoka, S.; Nakahama, S. *Tetrahedron Lett.* **2001**, *42*, 8645. Introduction of a butyl substituent was very effective to achieve the sufficient solubility of a series of oligo(1,3-adamantane)s.

(16) Selected data for **2**: ^{1}H NMR (C_6D_6, 300 MHz): 0.89 (t, $J = 7.1$ Hz, 3H, $\mathrm{CaH_3}$), 1.09−1.29 (m, 10H, $\mathrm{C}H_2\mathrm{C}H_2\mathrm{C}H_2\mathrm{CH_3}$, one of $\mathrm{C4H_2}$, one of $\mathrm{C8H_2}$, one of $\mathrm{C9H_2}$, one of $\mathrm{C10H_2}$), 1.63 (s, 2H, $\mathrm{C6H_2}$), 1.73 (d, $J = 10.4$ Hz, one of $\mathrm{C4H_2}$ and one of $\mathrm{C9H_2}$), 1.86 (d, $J = 10.4$ Hz, 2H, one of $\mathrm{C8H_2}$ and one of $\mathrm{C10H_2}$), 1.97−2.05 (2d, 2H, $\mathrm{C2H_2}$), 2.81 (s, 1H, C7H). ^{13}C NMR (C_6D_6, 75 MHz): 14.4 (Ca), 24.2 (Cb), 27.8 (Cc), 36.1 (C1, C3), 37.8 (Cd), 42.6 (C6), 45.3 (C8, C10), 48.1 (C-2), 49.8 (C4, C9), 53.5 (C7), 64.4 (C5).

(17) 1-Acetoxyadamantanes, 1,3-adducts of acetic acid, and unreacted **1** or **2** were observed in the reaction mixture after quenching the polymerization with acetic acid.

(18) Even tetramer of adamantane is hardly soluble in any organic solvent. See ref 15.

(19) Selected data for poly(**1**) obtained by cationic polymerization: IR (KBr): 2926, 2903, and 2852 (C−H), 1449 and 1348 cm^{-1} (C−H). Anal. calcd for $(C_{10}H_{14})_n$: C, 89.49; H; 10.51; found: C, 84.08; H, 9.98.

(20) Although the poly(**2**)s with M_ns lower than 2000 were readily soluble in THF, the poly(**2**)s having higher M_n values became partially insoluble in THF but completely soluble in 1,2-dichlorobenzene at 80 °C.

(21) Selected data for poly(**2**): ^{1}H NMR (1,2-dichlorobenzene/C_6D_6, = 10/1, 300 MHz): 0.93 (bs, 3H, CH_3), 1.2−1.6 (m, 18H, $\mathrm{C}H_2\mathrm{C}H_2\mathrm{C}H_2\mathrm{CH_3}$, $\mathrm{C2H_2}$, $\mathrm{C4H_2}$, $\mathrm{C6H_2}$, $\mathrm{C8H_2}$, $\mathrm{C9H_2}$, $\mathrm{C10H_2}$), 2.16 (bs, 1H, C7H); ^{13}C NMR (1,2-dichlorobenzene/C_6D_6, = 10/1, 75 MHz): 14.2 (Ca), 24.1 (Cb), 25.3 (Cc), 30.6 (C7), 34.0 (overlapped, C2 and C5), 35.7 (C8, C10) 38.5 (C1, C3), 41.4 (C4, C9), 42.4 (C6), 45.3 (Cd). IR (KBr): 2926 and 2854 (C−H), 1453, and 1348 cm^{-1} (C−H). Anal. calcd for $(C_{14}H_{22})_n$: C, 88.35; H; 11.65; found: C, 87.17; H, 11.47.

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(23) Unpublished result. The molecular weight of poly(**2**) was independently estimated by the comparison with a series of oligo(5-butyl-1,3-adamantane)s synthesized by the Wurtz-type coupling reaction of 3-butyl-1-bromoadamantane or 5,5′-dibutyl-3-dibromo-1,1′-biadamantane.

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