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# Cationic Ring-Opening Polymerization of 1,3-Dehydroadamantanes

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**Summary:** Ring-opening polymerizations of [3.3.1]propellane derivatives, 1,3-dehydroadamantane (**1**) and 5-butyl-1,3-dehydroadamantane (**2**), were carried out with $CF_3SO_3H$ in $CH_2Cl_2$ at 0 °C for 6–42 h. The central σ-bonds in **1** and **2** were exclusively opened to afford novel poly([3.3.1]propellane)s, poly(1,3-adamantane)s, in 52–95% yields. The resulting poly(**2**) possessing flexible butyl substituent was soluble in chloroform, THF, and 1,2-dichlorobenzene, and the degree of polymerization was estimated to be greater than 30, while the poly(**1**) was hardly soluble in the common organic solvents. All aliphatic poly(**1**) and poly(**2**) showed high thermal stability, their 10% weight loss temperatures were 421 and 486 °C, respectively.

**Keywords:** 1,3-dehydroadamantane; cationic polymerization; poly(1,3-adamantane); ring-opening polymerization; thermal stability

## Introduction

Small ring propellanes are highly strained and reactive hydrocarbons involving a tricyclic system fused by three methylene rings.[1,2] They are categorized into [1.1.1]-, [2.2.2]-, and [2.2.1]propellanes from the skeleton of tricyclic system. These highly strained molecules readily react with various chemical reagents to afford the corresponding ring-opening products. From the viewpoint of polymer chemists, they are considered to be typical cyclic monomers showing the ring-opening polymerizability. However, the study on the polymerization of propellanes is very limited, since they are usually too reactive and hard to synthesize or handle. Only the ring-opening polymerization of several [1.1.1]propellane derivatives has been so far reported.[3–6]

1,3-Dehydroadamantane, **1**, has a framework of [3.3.1]propellane.[7,8] This hydrocarbon possessing a strained cyclopropane ring can be synthesized from 1,3-dibromoadamantane in a good yield and shows a sufficient stability even after the isolation. An inverted 1,3-carbon-carbon bond of **1** undergoes the free-radical and electrophilic ring-opening reactions to afford 1,3-disubstituted adamantanes, indicating the high reactivity as the small ring propellane. It is reported that an insoluble polymeric product is formed by heating of **1** at 130–160 °C.[7] This thermally-obtained product is supposed to be a poly(1,3-adamantane) only by IR spectroscopy and elemental analysis, since the poor solubility has precluded its detailed characterization such as NMR spectroscopy, size exclusion chromatography (SEC), and viscosity measurements.

We have recently focused on the synthesis of the poly(1,3-adamantane) containing bulky and rigid adamantyl skeletons (Figure 1).[9] The synthetic routes of poly(1,3-adamantane)s involved a ring-opening polymerization of 1,3-dehydroadamantane derivatives or a coupling reaction of 3,3′-dibromo-biadamantanes (Scheme 1).[10,11] We have designed and polymerized a new 1,3-dehydroadamantane derivative, 5-butyl-1,3-dehydroadamantane, **2**, under the various polymerization conditions.[12] The introduction of a flexible butyl substituent

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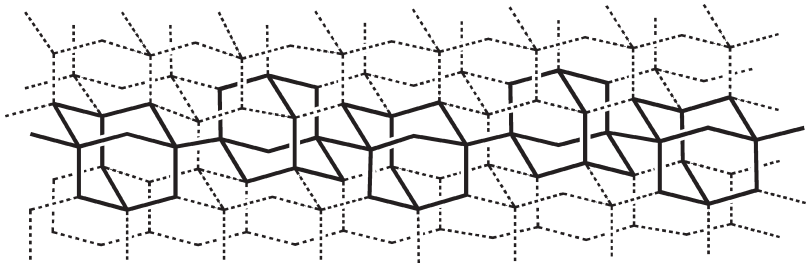


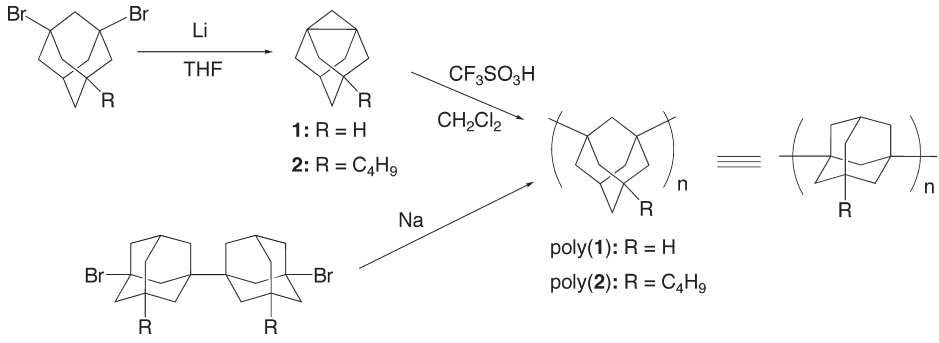
***Figure 1.***
Structure of poly(1,3-adamantane) in diamond lattice.

was very effective to increase the solubility of the resulting polymer and enabled to characterize the structure of soluble polymer in detail. In this paper, the cationic polymerizability of **1** and **2** is shown in addition to the thermal properties of the resulting polymers.

## Results and Discussion

Cyclic monomers, **1** and **2**, were synthesized by the reaction of 1,3-dibromoadamantane or 5-butyl-1,3-dibromoadamantane with lithium metal in THF at room temperature under argon atmosphere. The intramolecular Wurtz type coupling reaction smoothly proceeded to form the central propellane bond, and the yields of **1** and **2** were 81 and 79%, respectively. The resulting dehydroadamantanes were purified by repeating vacuum distillations on a vacuum line and were diluted with $CH_2Cl_2$ or THF. The dehydroadamantanes were very stable in a sealed tube in the solutions at least for several months, and no degradation was observed. However, they easily reacted with oxygen to give the copolymeric products containing a peroxide linkage, as previously reported.[7] We therefore dealt with **1** and **2** to prevent the oxidation in the all-glass apparatus under argon atmosphere or high vacuum conditions.

At first, we carried out the thermal polymerization of **1** in bulk at 80 °C for 72 h. A polymeric product was obtained in 83% yield after quenching with acetic acid. The resulting polymer was insoluble in any organic solvent,[13] as previously reported. We next attempted to cationically polymerize **1** with $CF_3SO_3H$ in $CH_2Cl_2$ at 0 °C for 6 h. White precipitate was formed in the reaction mixture during the course of the polymerization. This cationic polymerization also gave the insoluble polymer in 95% yield. By contrast, the reaction of **1** with either *n*-butyllithium or phenylmagnesium chloride in THF at room temperature gave no polymeric products, but the starting




***Scheme 1.***

monomer was recovered quantitatively.[14] This clearly shows that no anionic polymerization of **1** occurs even with the strong nucleophilic reagents. This lack of polymerizability of **1** under the anionic conditions is probably due to the high electron density of the carbon-carbon bond in the [3.3.1]propellane monomer, while the anionic polymerization of several [1.1.1]propellane derivatives has been reported.[3–6] We have thus clarified that the thermal or the cationic polymerization of **1** proceeds to provide the poly(**1**) in a good to quantitative yield, while its poor solubility still prohibits further characterization.[13]

We next employed monomer **2**, another 1,3-dehydroadamantane derivative possessing the flexible butyl substituent, for the various polymerizations. The cationic polymerization of **2** was carried out with $CF_3SO_3H$ in $CH_2Cl_2$ at 0 °C for 6 h. A white precipitate formed in the solution within several minutes, and the polymerization proceeded in a heterogeneous system. A polymer in the form of white powder was obtained in good yield after pouring the reaction mixture into methanol. In the case of **2**, the radical polymerization with AIBN in bulk proceeded as well as the thermal polymerization. By contrast, no reaction of **2** occurred with either *n*-butyllithium or phenylmagnesium chloride similar to the case of **1**. These polymerization behaviors of **2** resemble with the polymerizability of **1** very much, as discussed above. In this study, we will focus on the cationic polymerization of **2**.

The polymer obtained with $CF_3SO_3H$ showed good solubility in various organic solvents such as chloroform, THF, and 1,2-dichlorobenzene. However, the solubility was certainly dependent on the observed molecular weights, as shown later. The poly(**2**) having $M_n$ value over 2,000 showed poor solubility and only soluble in 1,2-dichlorobenzene at elevated temperature of 80 °C. We thus characterized the structure of the resulting polymer by using $^1H$ and $^{13}C$ NMR as well as IR spectroscopies and elemental analysis, although the solubility of high molecular weight sample was limited. Both the $^1H$ 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**). Figure 2 shows the $^{13}C$ NMR spectra of **2** and poly(**2**) obtained with $CF_3SO_3H$ along with 1-butyladamantane as a reference. In the spectra of 1-butyladamantane and **2**, eight and eleven carbon signals expected to the molecular symmetries are observed, respectively. The signals of adamantyl skeletons of **2** dramatically shift from those of 1-butyladamantane toward the downfield region except for one methylene carbon away from the propellane bond. On the other hand, after the polymerization of **2**, most of the signals corresponding to adamantane skeleton again move to upfield region, where the signals of 1-butyladamantane are located. In fact, eleven signals are again detected in the spectrum of poly(**2**), while one of the adamantyl methylene carbon and quaternary carbon substituted with butyl group are overlapped at 34.0 ppm. It is suggested that the drastic change of electronic environment certainly occurs through the ring-opening polymerization of highly strained dehydroadamantane derivative. Most importantly, the characteristic signal of inverted quaternary carbon of **2** at 36.1 ppm completely disappears after the polymerization. New signal corresponding to the quaternary carbons of main chain linkage in the internal adamantyl repeating unit appears at 38.5 ppm. Thus, the introduced butyl substituent enables the thorough characterization of poly(**2**) in the solution because of the improved solubility of the polymer. The drastic changes in the $^{13}C$ NMR measurement strongly indicate that the ring-opening polymerization of **2** exclusively occurs to afford a poly(5-butyl-1,3-adamantane) by breaking 1,3-propellane bond. This also suggests a similar chemical structure of poly(**1**) consisted of adamantane-1,3-diyl linkage via the ring-opening polymerization of **1**, although the detailed characterization of the resulting polymer is prevented by the low solubility.

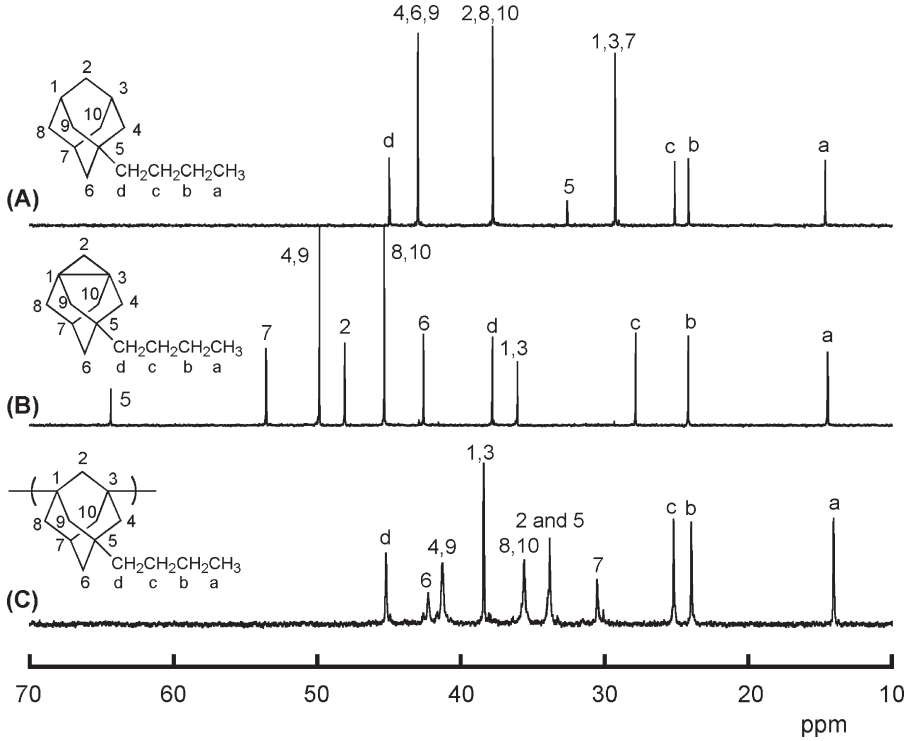



***Figure 2.***
$^{13}C$ NMR spectra of 1-butyladamantane in $CDCl_3$ (A), **2** in $C_6D_6$ (B), and poly(**2**) in 1,2-dichlorobenzene/$C_6D_6$ (10/1) (C).

Table 1 shows the polymerization result of **2**. When **2** was reacted with $CF_3SO_3H$ in $CH_2Cl_2$ at −78 °C, no polymerization occurs even after 24 h. On the other hand, the polymerization of **2** readily proceeded at 0 °C under the similar reaction conditions. The polymer yields reached 80–90% within 6 h, when the polymerization was carried out at the low monomer to initiator ratios (M/I). The rate of polymerization of **2** became slower at a higher feed ratio of M/I = 46, and the polymer yield was still 52%

***Table 1.***
Cationic polymerization of 1 and 2 in $CH_2Cl_2$[a)]

| Monomer | $CF_3SO_3H$ | M/I[b)] | temperature | time | yield[c)] | $10^{-3}M_n$[d)] | $M_w/M_n$[d)] | $T_{10}$[e)] |
|---|---|---|---|---|---|---|---|---|
| mmol | mmol | | °C | h | % | | | °C |
| **1**, 3.39 | 0.41 | 8.3 | 0 | 6 | 95[f)] | [g)] | [g)] | 421 |
| **2**, 3.50 | 0.18 | 19 | −78 | 24 | 0 | – | – | – |
| **2**, 2.85 | 0.52 | 5.5 | 0 | 6 | 89 | 1.5 | 1.30 | 445 |
| **2**, 7.70 | 0.36 | 21 | 0 | 6 | 78 | 3.2 | 1.43 | 472 |
| **2**, 8.66 | 0.19 | 46 | 0 | 6 | 52 | 4.4 | 1.56 | 485 |
| **2**, 8.66 | 0.19 | 46 | 0 | 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 from 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.

after 6 h. After the elongated reaction for 42 h, the yield reached 72% under the similar conditions.

The size exclusion chromatography (SEC) of poly(**2**) was measured in THF at 40 °C in the cases of low-molecular weight samples. For the SEC analysis of high-molecular weight samples, 1,2-dichlorobenzene was employed as the eluent at 135 °C. The SEC curve of polymer was unimodal in each solvent, and the polydispersity indices, $M_w/M_n$, were 1.3–1.6. Figure 3 shows the SEC curves of a series of poly(**2**) measured in 1,2-dichlorobenzene. The SEC curves shift toward higher molecular weight side as the M/I ratios increase from 6 to 21, and 46. The $M_n$ value estimated by using polystyrene standards reached 6000 at 72% yield,[15] when the polymerization was performed at M/I = 46. The observed molecular weights of poly(**2**) could be controlled to some extent by the feed molar ratio of monomer to initiator. This means that the cationic ring-opening polymerization of **2** proceeds smoothly and involves only minor proportion of chain transfer and termination reactions. This is in sharp contrast to the polymerization behavior of isobutene, where the propagating tertiary carbocation easily decomposes to provide a proton and a dead polymer having a terminal C=C moiety.[16,17] We consider that a propagating species, 1-adamantyl triflate,[18] at the bridgehead carbon of adamantane ring is remarkably stable during the course of the polymerization. This is supported by the unusual stability of non-planar 1-adamantyl carbocation due to the hyperconjugation effect through the rigid adamantyl skeleton, as previously pointed out.[19–21] In addition, 1,2-elimination of 1-adamantyl cation is strongly prevented, since the resulting alkene, adamantene, is highly distorted, if produced.[22–24]

Glass transition temperatures ($T_g$) of polymers were determined by the DSC measurement. In the case of poly(**1**), no glass transition behavior was observed below 300 °C before thermal degradation. On the other hand, the cationically synthesized poly(**2**) of $M_n = 6{,}000$ showed a $T_g$ around 205 °C. The introduced butyl substituent certainly decreased the softening points of poly(1,3-adamantane)s, while the observed $T_g$ value of poly(**2**) was still fairly

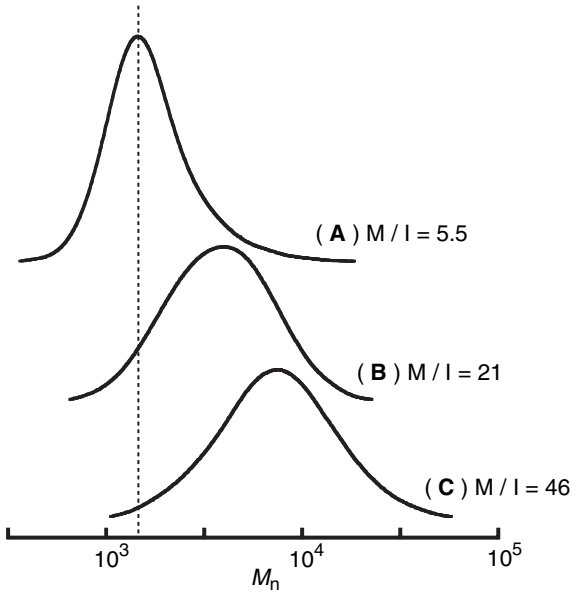



***Figure 3.***
SEC curves of poly(**2**)s measured in 1,2-dichlorobenzene at 135 °C. Peak A; run 3, $M_n = 1500$, $M_w/M_n = 1.30$: Peak B; run 4, $M_n = 3200$, $M_w/M_n = 1.43$: Peak C; run 6, $M_n = 6000$, $M_w/M_n = 1.56$.

high regardless of the saturated hydrocarbon structure.

The thermal stability of poly(**1**) and poly(**2**) was analyzed by the TGA measurement under nitrogen atmosphere. The poly(**1**) and poly(**2**) showed 10% weight loss at 421 and 486 °C, respectively. The polymers completely decomposed over 580 °C without forming residual ashes. It is considered that this observed high thermal stability of these all aliphatic polymers mainly derives from the rigid adamantane skeletons. In addition, the bridgehead carbon-carbon bond between the bulky adamantane rings is fairly stable.

In conclusion, we have succeeded in the synthesis of poly(1,3-adamantane)s via the cationic ring-opening polymerizations of [3.3.1]propellane derivatives, 1,3-dehydroadamantanes. The introduction of butyl substituent into the monomer is very effective to increase the solubility of the resulting polymer. The resulting all aliphatic poly(1,3-adamantane)s show high thermal stability in the TGA measurements.

## Experimental

### Materials

Commercially available 1-bromoadamantane, 1,3-dibromoadamantane, and $CF_3SO_3H$ were used without further purification. 1,3-Dehydroadamantane (**1**) was prepared by the reaction of 1,3-dibromoadamantane with lithium in THF in 81% yield. 1-Butyladamantane was prepared from 1-bromoadamantane and butylmagnesium bromide in $CH_2Cl_2$ in 65% yield. Bromination of 1-butyladamantane with bromine in the presence of $AlBr_3$ gave 1,3-dibromo-5-butyladamantane in 71% yield.

### Synthesis of 2

A mixture of 5-butyl-1,3-dibromoadamantane (11.1 g, 31.7 mmol) and lithium (1.00 g, 145 mmol) in dry THF (50 mL) was reacted at room temperature for 24 h under argon. The resulting solution was transferred into a round bottom flask equipped with a breakseal, and most of THF was removed on a vacuum line. The residue was sealed off under high vacuum condition. Repeating distillations gave 5-butyl-1,3-dehydroadamantane (**2**, 4.78 g, 25.2 mmol) in 79% yield. The resulting monomer was diluted with dry $CH_2Cl_2$ or heptane in an ampoule equipped with a breakseal. Selected data for **2**: $^1$H NMR ($C_6D_6$, 300 MHz): 0.89 (t, $J = 7.1$ Hz, 3H, $CaH_3$), 1.09–1.29 (m, 10H, $CH_2CH_2CH_2CH_3$, one of $C4H_2$, one of $C8H_2$, one of $C9H_2$, one of $C10H_2$), 1.63 (s, 2H, $C6H_2$), 1.73 (d, $J = 10.4$ Hz, one of $C4H_2$ and one of $C9H_2$), 1.86 (d, $J = 10.4$ Hz, 2H, one of $C8H_2$ and one of $C10H_2$), 1.97–2.05 (2d, 2H, $C2H_2$), 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).

### Polymerization

All reactions and polymerizations of **1** and **2** were carried out in an all-glass apparatus equipped with breakseals under high vacuum conditions. A typical procedure of cationic polymerization was as follows.

A $CH_2Cl_2$ solution of **2** (0.773M, 9.96 mL, 7.70 mmol) was added to $CF_3SO_3H$ (0.120M, 3.02 mL, 0.362 mmol) in $CH_2Cl_2$ at 0 °C. The reaction was continued for 6 h and quenched by the addition of acetic acid. The polymerization system was poured into methanol to precipitate a polymer. Filtration gave a poly(**2**) (1.14 g, 78%) as a white powder. The polymerization of **1** was similarly performed. The following is the selected data for poly(**1**) and poly(**2**).

**Poly(1):** IR (KBr): 2926, 2903, and 2852 (C–H), 1449 and 1348 (C–H) cm$^{-1}$. Anal calcd for $(C_{10}H_{14})_n$ : C, 89.49; H; 10.51; found: C, 84.08; H, 9.98.

**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, $CH_2$,$CH_2$,$CH_2CH_3$, $C2H_2$, $C4H_2$, $C6H_2$, $C8H_2$, $C9H_2$, $C10H_2$), 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 (C–H) $cm^{-1}$; Anal calcd for $(C_{14}H_{22})_n$: C, 88.35; H; 11.65; found: C, 87.17; H, 11.47.

**Measurements**

SEC chromatograms for determination of $M_n$ and $M_w/M_n$ values of polymers were obtained with a Waters 150CV instrument equipped with three polystyrene gel columns (ShodexAT-803MS × 2 + ShodexAT-803S) with a refractive index detection using 1,2-dichlorobenzene as an eluent at 135 °C at a flow rate of 1.0 mL $min^{-1}$. Polystyrene standards were used for the calibration. The NMR spectra were recorded on a Bruker DPX300 (300 MHz for $^1H$ and 75 MHz for $^{13}C$) either in $CDCl_3$ or in 1,2-dichlorobenzene/$C_6D_6$. IR spectra (KBr or NaCl disk) were recorded on a JASCO FT-IR 460 spectrophotometer. The $T_g$ values of polymers were measured by a Seiko Instrument DSC6220 instrument with heating rate of 10 °C $min^{-1}$ under nitrogen. A Seiko Instrument TG/DTA6200 was used for TGA analysis between 30 and 600 °C with heating rate of 10 °C $min^{-1}$ under nitrogen.

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[15] 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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