Cationic Ring-Opening Polymerization of Novel 1,3-Dehydroadamantanes with Various Alkyl Substituents: Synthesis of Thermally Stable Poly(1,3-adamantane)s

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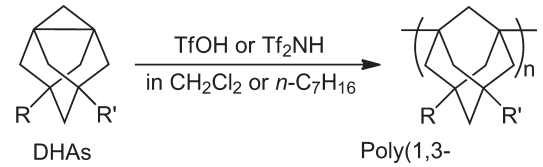
ABSTRACT: Cationic ring-opening polymerizations of 5-alkyl- or 5,7-dialkyl-1,3-dehydroadamantanes, such as 5-hexyl- (**4**), 5-octyl- (**5**), 5-butyl-7-isobutyl- (**6**), 5-ethyl-7-hexyl- (**7**), and 5-butyl-7-hexyl-1,3-dehydroadamantane (**8**), were carried out with super Brønsted acids, such as trifluoromethanesulfonic acid or trifluoromethanesulfonimide in CH_2Cl_2 or *n*-heptane. The ring-opening polymerizations of inverted carbon–carbon bonds in **4–8** proceeded to afford corresponding poly(1,3-adamantane)s in good to quantitative yields. Poly(**4–8**)s possessing alkyl substituents were soluble in 1,2-dichlorobenzene, although a nonsubstituted poly(1,3-adamantane) was not soluble in any organic solvent. In particular, poly(**8**) exhibited the highest molecular weight at around 7500 g mol^{-1} and showed excellent solubility in common organic solvents, such as THF, $CHCl_3$, benzene, and hexane. The resulting poly(**4–8**)s containing adamantane-1,3-diyl linkages showed good thermal stability, and 10% weight loss temperatures (T_{10}) were observed over 400 °C. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2013**, *51*, 4111–4124

KEYWORDS: cationic polymerization; 1,3-dehydroadamantane; poly(1,3-adamantane); ring-opening polymerization; thermal properties

INTRODUCTION 1,3-Dehydroadamantane (**1**),[1] a unique highly strained cage hydrocarbon,[2–6] is a typical [3.3.1]propellane derivative[6,7] and exhibits high reactivity toward various chemical reagents.[1,8] For example, **1** reacted with acetic acid or sulfuric acid to give a strain-free 1,3-disubstituted adamantane derivative via ring-opening reaction of its cyclopropane ring. From the viewpoint of polymer chemistry, **1** can be regarded as a reactive cyclic monomer to give a polymer containing an adamantane-1,3-diyl framework in its backbone. In fact, when **1** was heated at 130–160 °C, white powder, supposed to be a poly(1,3-adamantane),[9] was obtained, but detailed characterization of the chemical structure and molecular weight was prohibited due to its insolubility.[8] An insoluble polymer was similarly produced by free-radical and cationic polymerization of **1**, although **1** was intact with nucleophilic reagents such as *n*-BuLi or C_6H_5MgCl.[10] On the other hand, the copolymer derived from **1** showed good solubility in various organic solvents. Soluble alternating copolymers containing adamantane-1,3-diyl linkages were obtained by the spontaneous copolymerization of **1** with electron-deficient vinyl monomers such as acrylonitrile or methyl acrylate.[11] These results clearly indicated the ring-opening polymerizability of **1** under various conditions, but the poor solubility of homopoly(**1**) still hindered its thorough characterization.

In order to increase the solubility of poly(1,3-adamantane)s, we newly synthesized 5-butyl- (**2**) and 5,7-dibutyl-1,3-dehydroadamantane (**3**) as examples of alkyl-substituted 1,3-dehydroadamantanes (DHAs) and investigated the polymerizability of **2** and **3** under various conditions.[10] Then, cationic, radical, and thermal polymerizability of **2** and **3** was confirmed, similar to **1**, but they remained intact toward nucleophiles. Since the resulting poly(**2**) showed sufficient solubility in organic solvents such as THF or $CHCl_3$, various chracterizations such as NMR and size exclusion chromatography (SEC) measurements were possible to clarify the unique structure of poly(1,3-adamantane) and the molecular weight. Interestingly, the poly(**3**) showed lower solubility than poly(**2**), whereas two butyl groups were installed on each monomer unit. By introducing the same butyl groups, we now suspect that the increasing symmetry of the repeating unit reduces the solubility of poly(1,3-adamantane)s, even if the substituents are flexible. Furthermore, the



1 : R, R' = H
2 : R = H, R' = C_4H_9
3 : R, R' = C_4H_9
4 : R = H, R' = C_6H_{13}
5 : R = H, R' = C_8H_{17}
6 : R = C_4H_9, R' = $CH_2CH(CH_3)_2$
7 : R = C_2H_5, R' = C_6H_{13}
8 : R = C_4H_9, R' = C_6H_{13}

SCHEME 1 Cationic ring-opening polymerization of DHAs.

solubility of poly(**2**)s was still very limited in the cases of high molecular weight samples ($M_n > 2000$ g mol^{-1}), since they were only soluble in 1,2-dichlorobenzene (ODCB) under heating.

In order to expand the range of polymerizable cyclic monomers, we herein synthesize a series of novel DHAs possessing various alkyl substituents (Scheme 1). We propose two molecular designs for varying the polymerizability and for further improvement of the solubility of poly(1,3-adamantane)s. One is the synthesizing of novel DHAs having flexible alkyl substituents longer than the butyl group. We actually prepared new 5-alkyl-substituted DHAs such as 5-hexyl- (**4**) and 5-octyl-1,3-dehydroadamantane (**5**) possessing flexible alkyl chains longer than **2**. The other is the synthesizing of novel DHAs possessing asymmetrical structures by introducing two different alkyl substituents at the 5- and 7-positions on DHA frameworks.[12] According to the latter design, we here synthesized three asymmetrical DHAs such as 5-butyl-7-isobutyl- (**6**), 5-ethyl-7-hexyl- (**7**), and 5-butyl-7-hexyl-1,3-dehydroadamantane (**8**). This paper describes the synthesis and the ring-opening polymerization of **4–8**, and the solubility and thermal stability of the resulting poly(1,3-adamantane)s are also discussed.

EXPERIMENTAL

Materials

Commercially available 1-iodoethane, 1-bromohexane, 1-bromooctane, 1-bromo-2-methylpropane, fluorobenzene, tetrabutylammonium bromide (Bu_4NBr), NaOH, carbon tetrabromide (CBr_4), 1-bromoadamantane, bromine, lithium (wire), aluminum (foil), magnesium, and MeOH were used without further purification. CH_2Cl_2 for polymerization solvent was distilled from CaH_2 under nitrogen and further distilled from CaH_2 on a vacuum line. Diethyl ether (Et_2O) was dried over $CaCl_2$, filtered off, and stored over sodium wire. THF was refluxed over sodium wire for 3 h, distilled over $LiAlH_4$ under nitrogen. 1-Butyladamantane and 1-bromo-3-butyladamantane were synthesized according to our previous report.[10]

Initiators

Commercially available trifluoromethanesulfonic acid (TfOH) was used without further purification and diluted with dry CH_2Cl_2. Trifluoromethanesulfonimide (Tf_2NH)[13] was distilled over P_2O_5 on a vacuum line and diluted with dry CH_2Cl_2. BF_3OEt_2 was distilled over CaH_2 on a vacuum line and diluted with dry CH_2Cl_2. α,α'-Azobisisobutyronitrile (AIBN) for radical polymerization was purified by recrystallization from MeOH.

Measurement

NMR spectra were recorded on a Bruker DPX300 (300 MHz for ^{1}H and 75 MHz for ^{13}C) either in $CDCl_3$ or C_6D_6. The chemical shifts were reported in ppm downfield relative to $CHCl_3$ ($\delta = 7.26$) or C_6H_6 ($\delta = 7.16$) for ^{1}H NMR and $CDCl_3$ ($\delta = 77.1$) or C_6D_6 ($\delta = 128.0$) for ^{13}C NMR as standards. IR spectra (KBr disk or ATR) were recorded on a JASCO FT-IR 460 spectrophotometer. A Seiko Instrument TG/DTA6200 was used for TGA analysis between 30 and 600 °C with heating rate of 20 °C min^{-1} under nitrogen. SEC traces for determination of M_n and M_w/M_n values of poly(**4**) were obtained with a TOSOH 8121HT instrument equipped with polystyrene gel columns (Shodex HT-806×2) with a refractive index detection using ODCB as an eluent at 140 °C at a flow rate of 1.0 mL min^{-1}. Polystyrene standards were used for the SEC calibration. M_n of poly(**5**) was determined by SEC using a JASCO co-2065 Plus equipped with polystyrene gel columns (Shodex GPC KF-805L+GPC K-804L) with refractive index detector (JASCO RI-1530) using $CHCl_3$ as an eluent at 40 °C at a flow rate of 1.0 mL min^{-1}. Polystyrene standards were used for the SEC calibration. M_n and M_w/M_n of poly(**6–8**)s were measured by SEC using a Viscotek TDL 302 equipped with three polystyrene gel columns (TOSOH TSKgelG5000H_{XL}+G4000H_{XL}+G3000H_{XL}) with refractive index detector using THF as an eluent at 40 °C at a flow rate of 1.0 mL min^{-1}. Polystyrene standards were used for the SEC calibration. The M_n of poly(**8**) (Run 20) was determined by right angle laser light scattering size exclusion chromatography (RALLS-SEC) using a Viscotek TDL 305 Triple Detecter Array equipped with three polystyrene gel column (TOSOH TSKgel GMH_{XL}×2 and TSKgel G2000H_{XL}) with triple detectors (RI, LS, and viscosity) in THF at 40 °C.

General Procedure A: Synthesis of 1-Alkyladamantanes and 1,3-Dialkyladamantanes

1-Ethyladamantane

A solution of 1-iodoethane (58 mL, 725 mmol) in 150 mL of Et_2O was added dropwise at 0 °C to magnesium (23.9 g, 983 mmol) activated with 1,2-dibromoethane in Et_2O (150 mL) under nitrogen. The reaction was continued with stirring at room temperature for 3 h. After completion of the reaction, the Et_2O solution of Grignard reagent was transferred to another flask to remove the residual magnesium. Et_2O was removed under vacuum to give a solid. 1-Bromoadamantane (31.4 g, 146 mmol) in CH_2Cl_2 (200 mL) was added to the solidified Grignard reagent under nitrogen, and then the mixture was refluxed for 3 h. After cooling, the reaction system was carefully poured into 2 N HCl at 0 °C and the layers

were separated. The aqueous layer was extracted with hexane three times. The combined organic layer was washed with water and dried over anhydrous $MgSO_4$. After filtration and evaporation, adamantane, corresponding reductive byproduct, was removed at 70 °C under vacuum condition (24 mmHg), and following vacuum distillation gave a pale red oil of 1-ethyladamantane (10.5 g, 63.9 mmol, 44%, bp 38–40 °C/2.5 mmHg). Ethyl group: $C(b)H_2C(a)H_3$.

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.75–0.80 (t, $J = 7.5$ Hz, 3H, $C(a)H_3$), 1.04–1.12 (q, $J = 7.7$ Hz, 2H, $C(b)H_2$), 1.44 (2s, 6H, $C(2)H_2$), 1.59–1.72 (m, 6H, $C(4)H_2$), 1.94 (s, 3H, C(3)H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 7.0$ (Ca), 28.9 (C3), 32.3 (C1), 36.8 (Cb), 37.5 (C4), 42.1 (C2). Anal. Calcd for $C_{12}H_{20}$: C, 87.73; H, 12.27. Found: C, 88.01; H, 12.03.

1-Hexyladamantane

The reaction was performed following general procedure A, starting from 1-bromoadamantane (27.0 g, 126 mmol) to yield 1-hexyladamantane as colorless oil (17.8 g, 80.8 mmol, 64%, bp 95–100 °C/0.50 mmHg). Hexyl group: $C(f)H_2C(e)H_2C(d)H_2C(c)H_2C(b)H_2C(a)H_3$.

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.83–0.87 (t, $J = 6.4$ Hz, 3H, $C(a)H_3$), 1.03–1.06 (m, 2H, $C(f)H_2$), 1.23–1.34 (m, 8H, $C(b)H_2$, $C(c)H_2$, $C(d)H_2$, $C(e)H_2$), 1.46–1.47 (2s, 6H, $C(2)H_2$), 1.61–1.73 (m, 6H, $C(4)H_2$), 1.87–2.00 (bs, 3H, C(3)H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.3 (Ca), 22.5 (Cb), 22.9 (Cc), 29.0 (C3), 30.5 (Cd), 32.2 (Ce), 32.4 (C1), 37.5 (C4), 42.7 (C2), 45.0 (Cf). IR (neat, cm^{-1}): 2899, 2848, 1451, 813, 723. HRMS (EI) m/z Calcd for $C_{16}H_{28}$ $[M]^+$ 220.2191, found 220.2193.

1-Octyladamantane

The reaction was performed following general procedure A, starting from 1-bromoadamantane (26.0 g, 121 mmol) to yield 1-octyladamantane as colorless oil (12.8 g, 51.5 mmol, 43%, bp 79–81 °C/0.20 mmHg). Octyl group: $C(h)H_2C(g)H_2C(f)H_2C(e)H_2C(d)H_2C(c)H_2C(b)H_2C(a)H_3$.

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.83–0.89 (t, $J = 6.2$ Hz, 3H, $C(a)H_3$), 1.02–1.05 (m, 2H, $C(h)H_2$), 1.22–1.33 (m, 12H, $C(b)H_2$, $C(c)H_2$, $C(d)H_2$, $C(e)H_2$, $C(f)H_2$, $C(g)H_2$), 1.45–1.46 (2s, 6H, $C(2)H_2$), 1.60–1.72 (m, 6H, $C(4)H_2$), 1.93 (bs, 3H, C(3)H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.3 (Ca), 22.6 (Cb), 22.9 (Cc), 29.0 (C3), 29.6 (Cd), 29.9 (Ce), 30.9 (Cf), 32.1 (Cg) 32.4 (C1), 37.5 (C4), 42.7 (C2), 45.0 (Ch). IR (neat, cm^{-1}): 2898, 2846, 1098, 973, 811, 721. HRMS (EI) m/z Calcd for $C_{18}H_{32}$ $[M]^+$ 248.2504, found 248.2505.

1-Ethyl-3-hexyladamantane

The reaction was performed following general procedure A, starting from 1-ethyl-3-bromoadamantane (24.8 g, 102 mmol) to yield 1-ethyl-3-hexyladamantane as colorless oil (16.7 g, 67.2 mmol, 66%, bp 70–75 °C/1.0 mmHg). Ethyl and hexyl groups: $C(b)H_2C(a)H_3$, $C(c)H_2C(d)H_2C(e)H_2C(f)H_2C(g)H_2C(h)H_3$.

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.79–0.84 (t, $J = 7.4$ Hz, 3H, $C(a)H_3$), 0.90–0.95 (t, $J = 6.5$ Hz, 3H, $C(h)H_3$), 1.09–1.17 (m, 6H, $C(2)H_2$, $C(b)H_2$, $C(c)H_2$), 1.27–1.47 (m, 16H, $C(4)H_2$, $C(8)H_2$, $C(9)H_2$, $C(10)H_2$, $C(d)H_2$, $C(e)H_2$, $C(f)H_2$, $C(g)H_2$), 1.61 (s, 2H, $C(6)H_2$), 2.03 (bs, 2H, C(5)H, C(7)H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 7.1 (Ca), 14.3 (Ch), 22.7, 22.9, 30.6, and 32.2 (Cd, Ce, Cf, Cg), 29.4 (C5, C7), 33.1 (C1, C3), 36.7 (Cb), 37.1 (C6), 41.8 and 42.4 (C4, C8, C9, C10), 45.8 (Cc), 47.3 (C2). IR (neat, cm^{-1}): 2958, 2896, 2844, 1449, 1379, 968, 723. Anal. Calcd for $C_{18}H_{32}$: C, 87.02; H, 12.98. Found: C, 86.87; H, 12.81.

1-Butyl-3-isobutyladamantane

The reaction was performed following general procedure A, starting from 1-bromo-3-butyladamantane (17.2 g, 63.4 mmol) to yield 1-butyl-3-isobutyladamantane as colorless oil (11.0 g, 44.3 mmol, 70%, bp 70–74 °C/0.50 mmHg). Butyl and isobutyl groups: $C(d)H_2C(c)H_2C(b)H_2C(a)H_3$, $C(e)H_2C(f)H(C(g)H_3)_2$.

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.87–0.91 (m, 9H, $C(a)H_3$, $C(g)H_3$), 1.03–1.07 (d, $J = 5.2$ Hz, 2H, $C(e)H_2$), 1.03–1.07 (m, 2H, $C(d)H_2$), 1.17 (s, 2H, $C(2)H_2$), 1.20–1.24 (m, 4H, $C(b)H_2$, $C(c)H_2$), 1.26–1.47 (m, 8H, $C(4)H_2$, $C(8)H_2$, $C(9)H_2$, $C(10)H_2$), 1.55–1.56 (2s, 2H, $C(6)H_2$), 1.67–1.75 (m, 1H, C(f)H), 1.96 (bs, 2H, C(5)H, C(7)H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.4 (Ca), 22.9 (Cf), 23.9 (Cb), 25.0 (Cc), 26.0 (Cg), 29.4 (C5, C7), 33.1 and 33.9 (C1, C3), 37.0 (C6), 42.3 and 42.8 (C4, C8, C9, C10), 44.5 (Cd), 48.3 (C2), 54.0 (Ce).

1-Butyl-3-hexyladamantane

The reaction was performed following general procedure A, starting from 1-bromo-3-butyladamantane (17.6 g, 64.9 mmol) to yield 1-butyl-3-hexyladamantane as colorless oil (13.0 g, 47.0 mmol, 72%, bp 102–107 °C/0.20 mmHg). Butyl and hexyl groups: $C(d)H_2C(c)H_2C(b)H_2C(a)H_3$, $C(e)H_2C(f)H_2C(g)H_2C(h)H_2C(i)H_2C(j)H_3$.

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.87–0.91 (m, 6H, $C(a)H_3$, $C(j)H_3$), 1.04–1.07 (m, 4H, $C(d)H_2$, $C(e)H_2$), 1.14 (s, 2H, $C(2)H_2$), 1.22–1.31 (m, 12H, $C(b)H_2$, $C(c)H_2$, $C(f)H_2$, $C(g)H_2$, $C(h)H_2$, $C(i)H_2$), 1.31–1.44 (m, 8H, $C(4)H_2$, $C(8)H_2$, $C(9)H_2$, $C(10)H_2$), 1.57 (s, 2H, $C(6)H_2$), 1.98 (bs, 2H, C(5)H, C(7)H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.3 and 14.4 (Ca, Cj), 22.6, 22.9, 23.9, 25.0, 30.5, and 32.2 (Cb, Cc, Cf, Cg, Ch, Ci), 29.4 (C5, C7), 33.0 and 33.1 (C1, C3), 37.1 (C6), 42.4 (C4, C8, C9, C10), 44.5 and 44.8 (Cd, Ce), 47.7 (C2). IR (neat, cm^{-1}): 2955, 2896, 2844, 725. HRMS (EI) m/z Calcd for $C_{20}H_{36}$ $[M]^+$ 276.2817, found 276.2817.

General Procedure B: Monobromination of Alkyl-Substituted Adamantanes

1-Bromo-3-ethyladamantane

The reaction was performed following synthesis of 1-bromo-3-butyladamantane.[10c] A mixture of 1-ethyladamantane (33.2 g, 202 mmol) and bromine (50 mL) was stirred at room temperature for 24 h. The reaction mixture was carefully poured into aqueous $NaHSO_3$ solution at 0 °C to quench excess amount of bromine. The aqueous layer was extracted with Et_2O three times. The organic layer was dried over anhydrous $MgSO_4$ and filtered. After evaporation of Et_2O, the residue was distilled *in*

vacuo to yield white crystal of 1-bromo-3-ethyladamantane (45.0 g, 185 mmol, 92%, bp 47–61 °C/1.0 mmHg, mp 34–36 °C). Ethyl group: $C(b)H_2C(a)H_3$.

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.77–0.82 (t, $J = 7.5$ Hz, 3H, $C(a)H_3$), 1.13–1.20 (q, $J = 7.7$ Hz, 2H, $C(b)H_2$), 1.45–1.46 (2s, 4H, $C(4)H_2$, $C(10)H_2$), 1.57–1.72 (m, 2H, $C(6)H_2$), 2.06 (s, 2H, $C(2)H_2$), 2.14 (bs, 2H, C(5)H, C(7)H), 2.22–2.33 (m, 4H, $C(8)H_2$, $C(9)H_2$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 7.1 (Ca), 32.9 (C5, C7), 35.3 (C6), 35.8 (Cb), 38.1 (C3), 40.1 (C4, C10), 48.8 (C8, C9), 53.7 (C2), 67.3 (C1). IR (neat, cm^{-1}): 2903, 2848, 1455, 1304, 1356, 996, 955, 889, 820, 726, 676.

1-Bromo-3-isobutyladamantane

The reaction was performed following general procedure B, starting from 1-isobutyladamantane (615 mg, 3.20 mmol) to yield 1-bromo-3-isobutyladamantane as pale yellow oil (850 mg, 3.13 mmol, 98%). Isobutyl group: $C(c)H_2C(b)H(C(a)H_3)_2$.

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.88–0.91 (d, $J = 6.7$ Hz, 6H, $C(a)H_3$), 1.04–1.06 (d, $J = 5.3$ Hz, 2H, $C(c)H_2$), 1.50–1.51 (2s, 4H, $C(4)H_2$, $C(10)H_2$), 1.60–1.73 (m, 3H, C(b)H, $C(6)H_2$), 2.11 (bs, 4H, $C(2)H_2$, C(5)H, C(7)H), 2.22–2.35 (m, 4H, $C(8)H_2$, $C(9)H_2$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.9 (Cb), 25.8 (Ca), 32.8 (C5, C7), 35.2 (C6), 41.1 (C4, C10), 48.9 (C8, C9), 53.0 (Cc), 54.6 (C2), 67.3 (C1). IR (neat, cm^{-1}): 2903, 2851, 1455, 1304, 1133, 974, 815, 735, 678.

1-Bromo-3-butyl-5-isobutyladamantane

The reaction was performed following general procedure B, starting from 1-butyl-3-isobutyladamantane (11.0 g, 44.3 mmol) to yield 1-bromo-3-butyl-5-isobutyladamantane as pale yellow oil (14.9 g, 45.5 mmol, 103%). Butyl and isobutyl groups: $C(d)H_2C(c)H_2C(b)H_2C(a)H_3$, $C(e)H_2C(f)H(C(g)H_3)_2$.

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.87–0.91 (m, 9H, $C(a)H_3$, $C(g)H_3$), 1.06–1.08 (d, $J = 5.3$ Hz, 2H, $C(e)H_2$), 1.09–1.30 (m, 6H, $C(b)H_2$, $C(c)H_2$, $C(d)H_2$), 1.33–1.50 (m, 4H, $C(6)H_2$, $C(10)H_2$), 1.55 (s, 2H, $C(4)H_2$), 1.63–1.73 (m, 1H, C(f)H), 2.00–2.26 (m, 7H, $C(2)H_2$, C(7)H, $C(8)H_2$, $C(9)H_2$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.3 (Ca), 23.0 (Cf), 23.7 (Cb), 25.0 (Cc), 25.8 (Cg), 32.8 (C7), 38.3 and 39.0 (C3, C5), 40.2 and 40.7 (C6, C10), 43.3 (Cd), 46.4 (C8), 48.5 (C4), 52.8, 53.7, and 54.2 (C2, C9, Ce), 67.8 (C1).

General Procedure C: Dibromination of 1-Alkyladamantanes with $Br_2/AlBr_3$

1,3-Dibromo-5-hexyladamantane

The reaction was performed according to our previous report.[10c] A mixture of 1-hexyladamantane (16.8 g, 76.2 mmol) and bromine (30 mL) was stirred at room temperature for 24 h to prepare 1-bromo-3-hexyladamantane. Aluminum foil (80 mg, 2.97 mmol) was reacted with bromine (10 mL) in another flask, and it was added dropwise to the bromine solution of 1-bromo-3-hexyladamantane at 0 °C. The reaction mixture was stirred at 0 °C for 3 h and was carefully poured into aqueous $NaHSO_3$ solution at 0 °C to quench excess amount of bromine. The aqueous layer was extracted with Et_2O three times. The combined organic layer was dried over anhydrous $MgSO_4$ and filtered. After evaporation of Et_2O, the residue was distilled *in vacuo* to yield yellow liquid of 1,3-dibromo-5-hexyladamantane (14.9 g, 39.4 mmol, 52%, bp 170–180 °C/0.70 mmHg). Hexyl group: $C(f)H_2C(e)H_2C(d)H_2C(c)H_2C(b)H_2C(a)H_3$.

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.84–0.88 (t, $J = 6.1$ Hz, 3H, $C(a)H_3$), 1.10–1.35 (m, 10H, $C(b)H_2$, $C(c)H_2$, $C(d)H_2$, $C(e)H_2$, $C(f)H_2$), 1.44 (bs, 2H, $C(6)H_2$), 2.03 (bs, 4H, $C(4)H_2$, $C(9)H_2$), 2.19–2.24 (m, 5H, C(7)H, $C(8)H_2$,$C(10)H_2$), 2.72–2.81 (m, 2H, $C(2)H_2$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.2 (Ca), 22.6 and 22.7 (Cb, Cc), 30.0 (Cd), 31.9 (Ce), 34.8 (C7), 38.7 (C6), 41.6 (C5), 42.8 (Cf), 46.7 (C8, C10), 52.0 (C4, C9), 58.7 (C2), 62.5 (C1, C3). IR (neat, cm^{-1}): 2925, 2855, 1454, 1322, 1310, 1138, 1126, 957, 828, 705.

1,3-Dibromo-5-octyladamantane

The reaction was performed following general procedure C, starting from 1-octyladamantane (12.1 g, 48.7 mmol) to yield 1,3-dibromo-5-octyladamantane as pale orange oil (3.46 g, 8.52 mmol, 17%) after purification with column chromatography (silica gel, hexane). Octyl group: $C(h)H_2C(g)H_2C(f)H_2C(e)H_2C(d)H_2C(c)H_2C(b)H_2C(a)H_3$.

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.86–0.90 (t, $J = 6.5$ Hz, 3H, $C(a)H_3$), 1.10–1.33 (m, 14H, $C(b)H_2$, $C(c)H_2$, $C(d)H_2$, $C(e)H_2$, $C(f)H_2$, $C(g)H_2$, $C(h)H_2$) 1.46–1.47 (2s, 2H, $C(6)H_2$), 2.05 (s, 4H, $C(4)H_2$, $C(9)H_2$), 2.18–2.30 (m, 5H, C(7)H, $C(8)H_2$, $C(9)H_2$), 2.75–2.87 (m, 2H, $C(2)H_2$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.3 (Ca), 22.7 and 22.8 (Cb, Cc), 29.4, 29.7, and 30.4 (Cd, Ce, Cf), 32.0 (Cg), 34.9 (C7), 38.8 (C6), 41.7 (C5), 41.7 (Ch), 46.7 (C8, C10), 52.1 (C4, C9), 58.7 (C2), 62.6 (C1, C3). IR (neat, cm^{-1}): 2925, 2853, 1455, 1322, 1310, 1138, 957, 829, 705.

1,3-Dibromo-5-ethyl-7-hexyladamantane

The reaction was performed following general procedure C, starting from 1-ethyl-3-hexyladamantane (17.9 g, 72.0 mmol) to yield 1,3-dibromo-5-ethyl-7-hexyladamantane as pale yellow oil (13.0 g, 32.0 mmol, 44%) after purification with column chromatography (silica gel, hexane). Ethyl and hexyl groups: $C(b)H_2C(a)H_3$, $C(c)H_2C(d)H_2C(e)H_2C(f)H_2C(g)H_2C(h)H_3$.

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.83–0.93 (m, 6H, $C(a)H_3$, $C(h)H_3$), 1.24–1.29 (m, 14H, $C(6)H_2$, $C(b)H_2$, $C(c)H_2$,$C(d)H_2$, $C(e)H_2$, $C(f)H_2$,$C(g)H_2$), 1.94–2.06 (m, 8H, $C(4)H_2$, $C(8)H_2$, $C(9)H_2$, $C(10)H_2$), 2.75 (s, 2H, $C(2)H_2$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 7.3 (Ca), 14.3 (Ch), 22.7, 22.8, 30.0, and 31.9 (Cd, Ce, Cf, Cg), 34.8 (Cb), 41.5 and 41.6 (C5, C7), 42.7 (Cc), 43.7 (C6), 51.3 and 51.7 (C4, C8, C9, C10), 58.3 (C2), 62.7 (C1, C3). IR (neat, cm^{-1}): 2926, 2853, 1457, 1332, 1313, 1156, 959, 882, 844, 749, 714.

1,3-Dibromo-5-butyl-7-hexyladamantane

The reaction was performed following general procedure C, starting from 1-butyl-3-hexyladamantane (4.58 g, 16.6 mmol) to yield 1,3-dibromo-5-butyl-7-hexyladamantane as pale yellow oil (4.41 g, 10.2 mmol, 61%) after purification

with column chromatography (silica gel, hexane). Butyl and hexyl groups: $C(d)H_2C(c)H_2C(b)H_2C(a)H_3$, $C(e)H_2C(f)H_2C(g)H_2C(h)H_2C(i)H_2C(j)H_3$.

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.81–0.99 (m, 6H, $C(a)H_3$, $C(j)H_3$), 1.12–1.40 (m, 18H, $C(6)H_2$, $C(b)H_2$, $C(c)H_2$, $C(d)H_2$, $C(e)H_2$, $C(f)H_2$, $C(g)H_2$, $C(h)H_2$, $C(i)H_2$), 1.90–2.10 (m, 8H, $C(4)H_2$, $C(8)H_2$, $C(9)H_2$, $C(10)H_2$), 2.73 (bs, 2H, $C(2)H_2$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.2 (Ca, Cj), 22.8 and 22.8 (Cb, Ci), 23.5 and 25.1 (Cg, Ch), 30.1 and 31.9 (Cc, Cf), 41.5 (C5, C7), 42.4 and 42.7 (Cd, Ce), 44.2 (C6), 51.7 (C4, C8, C9, C10), 58.3 (C2), 62.8 (C1, C3). IR (neat, cm^{-1}): 2927, 2856, 1457, 1313, 1156, 974, 843, 714.

1,3-Dibromo-5-butyl-7-isobutyladamantane

The reaction was performed according to previous literature.[14,15] A suspension of 1-bromo-3-butyl-5-isobutyladamatnane (14.9 g, 45.5 mmol), CBr_4 (100 g, 302 mmol), Bu_4NBr (1.48 g, 4.59 mmol), aqueous NaOH (50wt %, 125 mL), and fluorobenzene (150 mL) was stirred at 70 °C. After 3 days, the reaction mixture was cooled to room temperature. The resultant suspension was neutralized with 2 N HCl and extracted with Et_2O. The combined organic layer was washed with 2 N HCl and dried over anhydrous $MgSO_4$. After filtration and removal of solvent *in vacuo*, the residue was purified by column chromatography (silica gel, hexane) to give 1,3-dibromo-5-butyl-7-isobutyladamantane as pale yellow oil (8.60 g, 21.2 mmol, 47%). Butyl and isobutyl groups: $C(d)H_2C(c)H_2C(b)H_2C(a)H_3$, $C(e)H_2C(f)H(C(g)H_3)_2$.

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.85–0.95 (m, 9H, $C(a)H_3$, $C(g)H_3$), 1.12–1.14 (d, $J = 5.4$ Hz, 2H, $C(e)H_2$), 1.18–1.30 (m, 8H, $C(b)H_2$, $C(c)H_2$, $C(d)H_2$, $C(6)H_2$), 1.62–1.79 (m, 1H, C(f)H), 1.92–2.09 (m, 8H, $C(4)H_2$, $C(8)H_2$, $C(9)H_2$, $C(10)H_2$), 2.72 (s, 2H, $C(2)H_2$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.2 (Ca), 23.1 (Cf), 23.5 (Cb), 25.0 (Cc), 25.7 (Cg), 41.4 and 42.1 (C5, C7), 42.4 (Cd), 44.6 (C6), 51.6 and 52.1 (C4, C8, C9, C10), 51.8 (Ce), 58.2 (C2), 62.6 (C1, C3).

General Procedure D: Synthesis of 1,3-Dehydroadamantanes

5-Hexyl-1,3-dehydroadamantane (4)

The reaction was performed according to our previous report.[10] A mixture of 1,3-dibromo-5-hexyladamantane (11.7 g, 30.9 mmol) and lithium (1.00 g, 144 mmol) in dry THF (60 mL) was reacted at room temperature for 24 h under argon. The resulting suspension was transferred into a round bottom flask equipped with a break-seal, and THF was thoroughly removed from the suspension on the vacuum line. The residue was sealed off under high vacuum conditions. Repeating vacuum distillations in the all-glass apparatus gave colorless oil of **4** (4.32 g, 19.8 mmol, 64%).[16] For the NMR measurement, the sample was diluted with C_6D_6. For ring-opening polymerization, the sample was diluted with CH_2Cl_2 or *n*-heptane. Hexyl group in **4** and poly(**4**): $C(f)H_2C(e)H_2C(d)H_2C(c)H_2C(b)H_2C(a)H_3$.

^{1}H NMR (300 MHz, C_6D_6): δ 0.89–0.93 (t, $J = 6.5$ Hz, 3H, $C(a)H_3$), 1.10–1.40 (m, 14H, $C(b)H_2$, $C(c)H_2$, $C(d)H_2$, $C(e)H_2$, $C(f)H_2$, one of $C(4)H_2$, one of $C(8)H_2$, one of $C(9)H_2$, one of $C(10)H_2$), 1.64 (s, 2H, $C(6)H_2$), 1.73–1.76 (d, $J = 10$ Hz, 2H, one of $C(4)H_2$, one of $C(9)H_2$), 1.85–1.88 (d, $J = 10$ Hz, 2H, one of $C(8)H_2$, one of $C(10)H_2$), 1.98–2.06 (m, 2H, $C(2)H_2$), 2.82 (bs, 1H, C(7)H). ^{13}C NMR (75 MHz, C_6D_6): δ 14.5 (Ca), 23.2 (Cb), 25.6 (Cc), 30.8 (Cd), 32.3 (Ce), 36.1 (C1, C3), 38.1 (Cf), 42.6 (C6), 45.3 (C8, C10), 48.1 (C2), 49.9 (C4, C9), 53.5 (C7), 64.4 (C5).

5-Octyl-1,3-dehydroadamantane (5)

The reaction was performed following general procedure D, starting from 1,3-dibromo-5-octyladamantane (4.93 g, 12.1 mmol) to yield **5** as colorless oil (2.17 g, 8.80 mmol, 73%). Octyl group in **5** and poly(**5**): $C(h)H_2C(g)H_2C(f)H_2C(e)H_2C(d)H_2C(c)H_2C(b)H_2C(a)H_3$.

^{1}H NMR (300 MHz, C_6D_6): δ 0.89–0.93 (t, $J = 6.4$ Hz, 3H, $C(a)H_3$), 1.11–1.40 (m, 18H, $C(b)H_2$, $C(c)H_2$, $C(d)H_2$, $C(e)H_2$, $C(f)H_2$, $C(g)H$, $C(h)H_2$, one of $C(4)H_2$, one of, $C(8)H_2$, one of $C(9)H_2$, one of C(10)), 1.65 (s, 2H, $C(6)H_2$), 1.73–1.77 (d, $J = 10$ Hz, 2H, one of $C(4)H_2$, one of $C(9)H_2$), 1.85–1.88 (d, $J = 10$ Hz, one of $C(8)H_2$, one of $C(10)H_2$), 1.95–2.05 (m, 2H, $C(2)H_2$), 2.82 (s, 1H, C(7)H). ^{13}C NMR (75 MHz, C_6D_6): δ 14.4 (Ca), 23.2 (Cb), 25.6 (Cc), 29.9 and 30.1 (Cd, Ce), 31.2 (Cf), 32.4 (Cg), 36.0 (C1, C3), 38.1 (Ch), 42.6 (C6), 45.3 (C8, C10), 48.0 (C2), 49.8 (C4, C9), 53.5 (C7), 64.4 (C5).

5-Butyl-7-isobutyl-1,3-dehydroadamantane (6)

The reaction was performed following general procedure D, starting from 1,3-dibromo-5-butyl-7-isobutyladamantane (8.35 g, 20.6 mmol) to yield **6** as colorless oil (3.41 g, 13.8 mmol, 67%). Butyl and isobutyl groups in **6** and poly(**6**): $C(d)H_2C(c)H_2C(b)H_2C(a)H_3$, $C(e)H_2C(f)H(C(g)H_3)_2$.

^{1}H NMR (300 MHz, C6D6): δ 0.89–0.95 (m, 9H, $C(a)H_3$, $C(g)H_3$), 1.01–1.10 (m, 4H, one of $C(4)H_2$, one of $C(8)H_2$, one of $C(9)H_2$, one of $C(10)H_2$), 1.20–1.29 (m, 8H, $C(b)H_2$, $C(c)H_2$, $C(d)H_2$, $C(e)H_2$), 1.58 (s, 2H, $C(6)H_2$), 1.63–1.72 (m, 5H, one of $C(4)H_2$, one of $C(8)H_2$, one of $C(9)H_2$, one of $C(10)H_2$, C(f)H), 1.93 (bs, 2H, $C(2)H_2$). ^{13}C NMR (75 MHz, C6D6): δ 14.4 (Ca), 24.2 (Cb), 25.0 (Cf), 25.3 (Cg), 27.9 (Cc), 34.8 (C1, C3), 37.6 (Cd), 46.5 (C2), 47.0 (Ce), 48.1 (C6), 49.0 and 50.0 (C4, C8, C9, C10), 63.5 (C5, C7).

5-Ethyl-7-hexyl-1,3-dehydroadamantane (7)

The reaction was performed following general procedure D, starting from 1,3-dibromo-5-ethyl-7-hexyladamantane (6.68 g, 16.4 mmol) to yield **7** as colorless oil (1.54 g, 6.23 mmol, 38%). Ethyl and hexyl groups in **7** and poly(**7**): $C(b)H_2C(a)H_3$, $C(c)H_2C(d)H_2C(e)H_2C(f)H_2C(g)H_2C(h)H_3$.

^{1}H NMR (300 MHz, C_6D_6): δ 0.82–0.87 (t, $J = 7.5$ Hz, 3H, $C(a)H_3$), 0.91–0.95 (t, $J = 6.4$ Hz, 3H, $C(h)H_3$), 1.06–1.14 (m, 4H, one of $C(4)H_2$, one of $C(8)H_2$, one of $C(9)H_2$, one of $C(10)H_2$), 1.26–1.43 (m, 12H, $C(b)H_2$, $C(c)H_2$, $C(d)H_2$, $C(e)H_2$, $C(f)H_2$,$C(g)H_2$,), 1.59 (s, 2H, $C(6)H_2$), 1.64–1.70 (m, 4H, one of $C(4)H_2$, one of $C(8)H_2$, one of $C(9)H_2$, one of $C(10)H_2$), 1.93 (s, 2H, $C(2)H_2$). ^{13}C NMR (75 MHz, C_6D_6): δ 9.8 (Ca), 14.5 (Ch), 23.2, 25.7, 30.0, 30.9, 32.9, and 37.9 (Cb, Cc, Cd,

TABLE 1 Cationic Polymerization of **4** and **5** in CH_2Cl_2[a]

Run	DHA	Initiator	M/I	Temperature (°C)	Time (h)	Yield[b] (%)	SEC in ODCB[c] $M_n \times 10^{-3}$	SEC in ODCB[c] M_w/M_n	T_{10}[d] (°C)
1	**4**	TfOH	25	30	1	100	2.9	1.60	450
2	**4**	TfOH	44	30	16	98	3.5	1.70	468
3	**4**	TfOH	116	30	18	90	3.4	1.90	457
4[e]	**4**	TfOH	56	30	16	78	4.1	2.00	465
5	**4**	Tf_2NH	21	−78	18	80	2.2	1.70	427
6	**4**	BF_3OEt_2	2.4	−78	90	88	1.8	1.50	441
7	**5**	TfOH	47	30	6	64	2.4[f]	1.62[f]	439
8	**5**	TfOH	39	30	24	77	2.8[f]	1.37[f]	462

[a] Quenched with MeOH.
[b] MeOH insoluble part.
[c] Measured in 1,2-dichlorobenzene calibrated by polystyrene standards.
[d] 10% weight loss temperature by TGA.
[e] Polymerization was carried out in $CHCl_3$.
[f] Measured in $CHCl_3$ calibrated by polystyrene standards.

Ce, Cf, Cg), 34.7 (C1, C3), 46.5 (C2), 47.3 (C6), 48.5 and 49.1 (C4, C8, C9, C10), 63.5 and 63.9 (C5, C7).

5-Butyl-7-hexyl-1,3-dehydroadamantane (8)

The reaction was performed following general procedure D, starting from 1,3-dibromo-5-butyl-7-hexyladamantane (4.47 g, 10.3 mmol) to yield **8** as colorless oil (1.52 g, 5.53 mmol, 54%). Butyl and hexyl groups in **8** and poly(**8**): $C(d)H_2C(c)H_2C(b)H_2C(a)H_3$, $C(e)H_2C(f)H_2C(g)H_2C(h)H_2C(i)H_2C(j)H_3$.

^{1}H NMR (300 MHz, C_6D_6): δ 0.89–0.93 (m, 6H, $C(a)H_3$, $C(j)H_3$), 1.04–1.14 (m, 4H, one of $C(4)H_2$, one of $C(8)H_2$, one of $C(9)H_2$, one of $C(10)H_2$), 1.20–1.35 (m, 16H, $C(b)H_2$, $C(c)H_2$, $C(d)H_2$, $C(e)H_2$, $C(f)H_2$, $C(g)H_2$, $C(h)H_2$, $C(i)H_2$), 1.60 (s, 2H, $C(6)H_2$), 1.66–1.70 (m, 4H, one of $C(4)H_2$, one of $C(8)H_2$, one of $C(9)H_2$, one of $C(10)H_2$), 1.95 (s, 2H, $C(2)H_2$). ^{13}C NMR (75 MHz, C6D6): δ 14.5 (Ca, Cj), 23.2, 24.2, 25.7, and 27.9 (Cb, Cg, Ch, Ci), 31.0 and 32.4 (Cc, Cf), 34.8 (C1, C3), 37.6 and 37.9 (Cd, Ce), 46.6 (C2), 47.9 (C6), 49.2 (C4, C8, C9, C10), 63.6 (C5, C7).

Ring-Opening Polymerization of DHAs

All polymerizations of DHAs were carried out in an all-glass apparatus equipped with break-seals under high vacuum conditions (10^{-6} mmHg).[16] Typical polymerization procedure was as follows.

Cationic Polymerization of 4

A CH_2Cl_2 solution of **4** (0.827 M, 4.8 mL, 3.97 mmol) was added to TfOH (0.0820 M, 1.1 mL, 0.0902 mmol) in CH_2Cl_2 at 30 °C (Table 1, Run 2). The reaction mixture was continued at 30 °C for 16 h and quenched with MeOH. The polymerization system was poured into MeOH to precipitate a polymer. Filtration gave a poly(**4**) (850 mg, 98%) as a white powder. The cationic polymerizations of **5–8** were similarly performed. The following was the selected spectral data for poly(**4–8**)s.

Poly(4)

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.89 (bs, 3H, $C(a)H_3$), 1.12–1.65 (br, 22H, $C(b)H_2$, $C(c)H_2$, $C(d)H_2$, $C(e)H_2$, $C(f)H_2$, $C(2)H_2$, $C(4)H_2$, $C(6)H_2$, $C(8)_2$, $C(9)H_2$, $C(10)H_2$), 2.01–2.25 (m, 1H, C(7)H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.2 (Ca), 22.8 (Cb), 23.0 (Cc), 30.1 (C7), 30.7 (Cd), 32.2 (C5), 33.4 (C2), 33.7 (Ce), 35.3 (C8, C10), 38.1 (C1, C3), 40.9 (C4, C9), 42.1 (C6), 45.6 (Cf). IR (KBr, cm^{-1}): 2926, 2854, 1450, 1351, 1086. Anal Calcd for $(C_{16}H_{26})_n$: C, 88.00; H, 12.00. Found: C, 86.72; H, 11.57.

Poly(5)

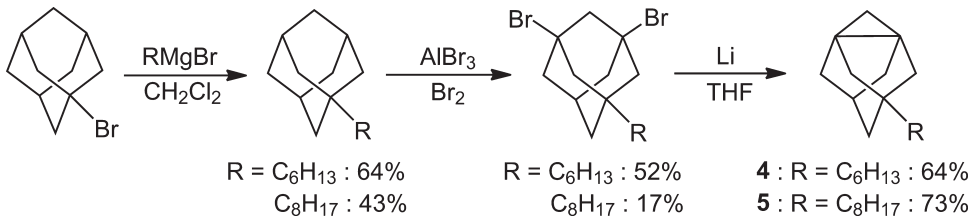
^{1}H NMR (300 MHz, $CDCl_3$): δ 0.88–0.92 (t, $J = 6.1$ Hz, 3H, $C(a)H_3$), 1.00–1.60 (br, 26H, $C(b)H_2$, $C(c)H_2$, $C(d)H_2$, $C(e)H_2$, $C(f)H_2$ $C(g)H_2$, $C(h)H_2$, $C(2)H_2$, $C(4)H_2$, $C(6)H_2$, $C(8)H_2$, $C(9)H_2$, $C(10)H_2$), 2.01–2.14 (br, 1H, C(7)H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.2 (Ca), 22.9 (Cb, Cc), 29.7 (Cd), 29.9 (Ce), 30.2 (C7), 31.1 (Cf), 32.1 (C5), 33.6 (C2), 33.7 (Cg), 35.3 (C8, C10), 38.2 (C1, C3), 40.9 (C4, C9), 42.1 (C6), 45.6 (Ch). IR (KBr, cm^{-1}): 2925, 2853, 1458, 1350. Anal Calcd for $(C_{18}H_{30})_n$: C, 87.73; H, 12.27. Found: C, 87.10; H, 12.43.

Poly(6)

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.90 (br, 9H, $C(a)H_3$, $C(g)H_3$), 1.10–1.55 (br, 20H, $C(b)H_2$, $C(c)H_2$, $C(d)H_2$, $C(e)H_2$, $C(2)H_2$, $C(4)H_2$, $C(6)H_2$, $C(8)H_2$, $C(9)H_2$, $C(10)H_2$), 1.72–1.74 (br, 1H, C(f)H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.4 (Ca), 23.0 (Cf), 24.0 (Cb), 25.1 (Cc), 26.2 (Cg), 33.1 (C2), 33.9 and 34.8 (C5, C7), 38.5 (C1, C3), 40.5 and 41.1 (C4, C8, C9, C10), 45.1 (Cd), 46.5 (C6), 54.5 (Ce). IR (KBr, cm^{-1}): 2952, 2927, 1466, 1364. Anal Calcd for $(C_{18}H_{30})_n$: C, 87.73; H, 12.27. Found: C, 87.20; H, 12.68.

Poly(7)

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.83 (bs, 3H, $C(a)H_3$), 0.90 (bs, 3H, $C(h)H_3$), 0.99–1.49 (br, 24H, $C(b)H_2$, $C(c)H_2$, $C(d)H_2$, $C(e)H_2$, $C(f)H_2$, $C(g)H_2$, $C(2)H_2$, $C(4)H_2$, $C(6)H_2$, $C(8)H_2$, $C(9)H_2$, $C(10)H_2$). ^{13}C NMR (75 MHz, $CDCl_3$) : δ 7.5 (Ca), 14.3 (Ch), 22.9 (Cg), 23.0 (Cf), 30.7 (Ce), 32.2 (C5, C7), 33.4 (C2), 34.0 (Cd), 38.7 (C1, C3), 37.1 (C8, C10), 40.1 (C4, C9), 40.7 (Cb), 45.3 (Cc), 45.9 (C6). IR (KBr, cm^{-1}): 2925, 2854, 1449, 1342. Anal Calcd for $(C_{18}H_{30})_n$: C, 87.73; H, 12.27. Found: C, 86.17; H, 11.95.



SCHEME 2 Synthesis of **4** and **5**.

Poly(8)

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.89–0.93 (br, 6H, C(a)H_3, C(j)H_3), 1.01–1.70 (br, 28H, C(b)H_2, C(c)H_2, C(d)H_2, C(e)H_2, C(f)H_2, C(g)H_2, C(h)H_2, C(i)H_2, C(2)H_2, C(4)H_2, C(6)H_2, C(8)H_2, C(9)H_2, C(10)H_2). ^{13}C NMR (75 MHz, $CDCl_3$) : δ 14.3 (Ca, Cj), 22.9 and 23.0 (Cb, Ci), 24.0 (Ch), 25.1 (Cg), 30.7 and 32.2 (Cc, Cf), 33.8 (C2), 34.1 and 34.2 (C5, C7), 38.8 (C1, C3), 40.8 (C4, C8, C9, C10), 45.1, 45.4 (Cd, Ce), 46.6 (C6). IR (KBr, cm^{-1}): 2926, 2855, 1466, 1337. Anal Calcd for $(C_{20}H_{34})_n$: C, 87.51; H,12.49. Found: C, 86.53; H, 12.97.

Radical Polymerization of 6

Radical polymerization of **6** (490 mg, 1.99 mol) was performed with AIBN (37.0 mg, 0.220 mmol) in bulk at 80 °C for 24 h (Run 24). The reaction mixture was cooled to room temperature and terminated with MeOH. The reaction system was diluted with THF and was poured into MeOH to precipitate a polymer (140 mg, 29%). The radical polymerization of **8** was similarly performed. The following is the selected data for poly(**6**) and poly(**8**) obtained by radical polymerization.

Poly(6-radical)

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.90 (bs, 9H, C(a)H_3, C(g)H_3), 1.04–2.06 (br, 21H, C(b)H_2, C(c)H_2, C(d)H_2, C(e)H_2, C(f)H, C(2)H_2, C(4)H_2, C(6)H_2, C(8)H_2, C(9)H_2, C(10)H_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.2 (Ca), 23.1 (Cf), 24.0 (Cb), 25.2 (Cc), 26.1 (Cg), 33.8–34.1 (C2), 34.7–35.3 (C5, C7), 38.4–38.7 (C1, C3), 40.3–42.0 (C4, C8, C9, C10), 44.8–45.1 (Cd), 47.2 (C6), 54.5–54.7 (Ce). IR (KBr, cm^{-1}): 2952, 2927, 1466, 1364. Anal Calcd for $(C_{18}H_{30})_n$: C, 87.73; H, 12.27. Found: C, 84.70; H, 12.51; N, 0.13.

Poly(8-radical)

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.86–0.90 (br, 6H, C(a)H_3, C(j)H_3), 1.02–1.60 (br, 28H, C(b)H_2, C(c)H_2, C(d)H_2, C(e)H_2, C(f)H_2, C(g)H_2, C(h)H_2, C(i)H_2, C(2)H_2, C(4)H_2, C(6)H_2, C(8)H_2, C(9)H_2, C(10)H_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.2, 14.3 (Ca, Cj), 22.8 and 22.9 (Cb, Ci), 24.0 (Ch), 25.2 (Cg), 30.7 and 32.2 (Cc and Cf), 33.9 (C2), 34.0 and 34.1 (C5, C7), 38.5 and 38.8 (C1, C3), 40.4–41.2 (C4, C8, C9, C10), 44.5–45.4 (Cd, Ce), 46.7 (C6). IR (KBr, cm^{-1}): 2926, 2855, 1466, 1341. Anal Calcd for $(C_{20}H_{34})_n$: C, 87.51; H, 12.49. Found: C, 86.20; H, 12.93; N, 0.25.

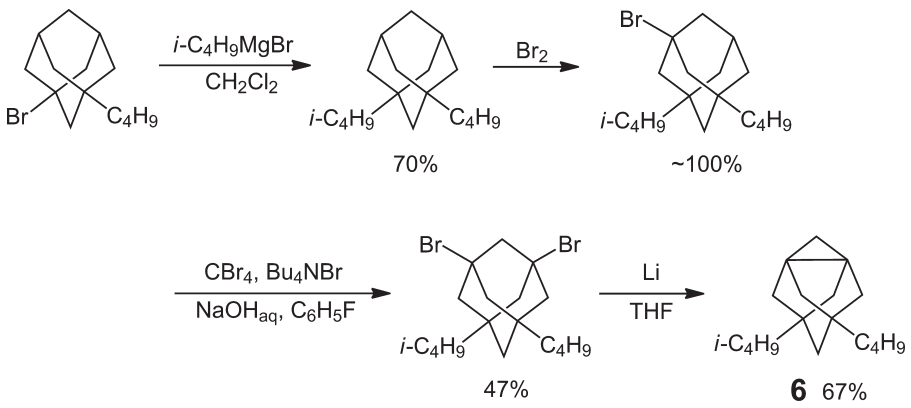
RESULTS AND DISCUSSION

Synthesis and Ring-Opening Polymerization of 5-Alkyl-1,3-dehydroadamantanes

5-Alkyl-substituted DHAs, **4** and **5**, were synthesized according to the reported procedure for **2** (Scheme 2).[10] First, 1-alkyladamantanes were prepared by the coupling reaction of alkylmagnesium bromide and 1-bromoadamantane in CH_2Cl_2.[17] Subsequent bromination of 1-alkyladamantanes with bromine in the presence of $AlBr_3$ gave the corresponding 1,3-dibromo-5-alkyladamantanes. The resulting 1,3-dibromoadamantanes were finally converted into 5-alkyl-DHAs, **4** and **5**, in 64–73% yield by treating with lithium in THF. Careful treatment under argon and vacuum distillation are necessary for DHAs to avoid copolymerization with oxygen.[8,18]

At first, we carried out cationic polymerization of **4** with TfOH at 30 °C in CH_2Cl_2 (Table 1, Run 1). A white precipitation formed within 5 min, and the polymerization was quenched with MeOH after 1 h. The white powdery solid was quantitatively obtained after precipitation into MeOH. Since the resulting polymer was not completely soluble in THF, we employed high-temperature SEC in ODCB for molecular weight measurement. The M_n of the resultant poly(**4**) was estimated to be 2900 g mol^{-1}, and the polydispersity index, M_w/M_n, was 1.60, indicating broad molecular weight distribution (MWD). This M_n value was lower than the calculated value ($M_n$calcd = 5500 g mol^{-1}), based on the molar ratio between monomer and initiator, assuming the mechanism of living polymerization. We then increased the feed molar ratio between monomer and initiator (M/I) to obtain a higher M_n polymer. Indeed, the M_ns of the resulting poly(**4**)s slightly increased, but were still lower than the expected values (Runs 2 and 3). Changing the solvent from CH_2Cl_2 to $CHCl_3$ also gave a similar polymerization result for **4**. We then attempted cationic polymerization of **4** with Tf_2NH[13] and BF_3OEt_2 in CH_2Cl_2 (Runs 5 and 6). When we mixed monomer solution with Tf_2NH or BF_3OEt_2 at −78 °C, a white precipitation instantaneously appeared and the polymerization system became a slurry. From the appearance of the polymerization system, initiation with Tf_2NH or BF_3OEt_2 might induce rapid propagation of **4** even at the low temperature of −78 °C. The poly(**4**)s obtained with Tf_2NH or BF_3OEt_2 were low molecular weight oligomers.

We similarly operated the ring-opening polymerization of **5** with TfOH in CH_2Cl_2 at 30 °C for 6 h (Run 7). Although we introduced an octyl group on **5**, longer than the butyl and hexyl groups, the polymerization system of **5** was still heterogeneous in CH_2Cl_2 as were those for **2** and **4**. After termination, poly(**5**) was isolated in 64% yield and the M_n was 2400 g mol^{-1}, estimated by SEC in $CHCl_3$. Although we prolonged the polymerization time for 24 h, the yield and M_n value only slightly increased (Run 8). Thus, two novel 5-



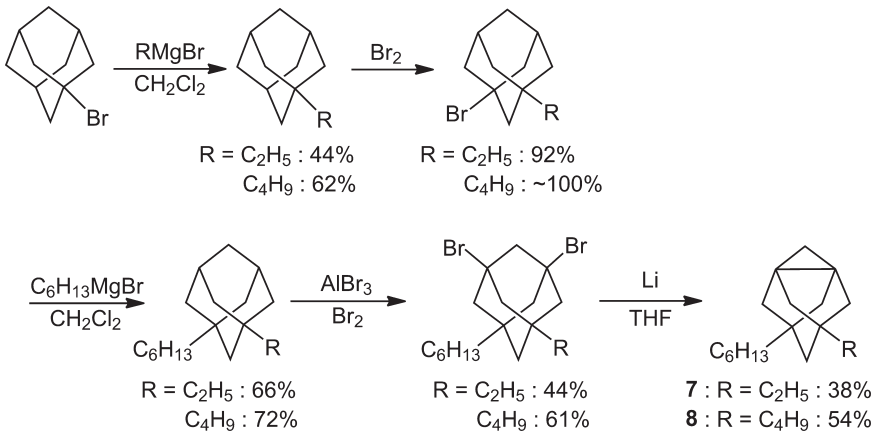
SCHEME 3 Synthesis of 6.

alkyl-DHAs of **4** and **5** showed ring-opening polymerizability, similar to that for **2**, to give poly(1,3-adamantane)s. The introduction of a longer alkyl chain such as a hexyl or octyl group on the adamantane skeleton did not remarkably improve the solubility of poly(1,3-adamantane)s compared with that of poly(**2**).

Synthesis and Ring-Opening Polymerization of 5,7-Dialkyl-1,3-dehydroadamantanes

Next, we attempted to synthesize new asymmetrical 5,7-dialkyl-substituted DHAs (**6–8**). Unfortunately, synthesis of **6** possessing branched isobutyl group was not achieved by normal synthetic pathway (Scheme 2),[10] since decomposition of isobutyl substituent occurred during the introduction of second bromine atom under harsh acidic condition with $AlBr_3/Br_2$. Then, we employed radical bromination with CBr_4 under basic condition[14,15] to synthesize 1,3-dibromoadamantane possessing isobutyl group. As a result, we successfully obtained **6** as shown in Scheme 3. On the other hand, asymmetrical DHAs bearing only linear alkyl substituents, **7** and **8**, were prepared according to the normal synthetic pathway for **2–5** without difficulty (Scheme 4).

At first, cationic polymerization of **6** was performed with TfOH in CH_2Cl_2 at 30 °C. A white precipitation formed during the polymerization of **6**, and poly(**6**) was obtained in 87% yield after 24 h. Interestingly, the resulting asymmetrical poly(**6**) was soluble in various solvents, including benzene, chloroform, and THF, while symmetrical poly(**3**), an isomer of poly(**6**), was insoluble in organic solvents. Therefore, the chemical structures and molecular weights of poly(**6**) could be characterized by ^1H and ^{13}C NMR and SEC measurements in solution states. In fact, the M_n of resultant poly(**6**) possessing isobutyl and butyl substituents was estimated to be 2200 g mol^{-1} by SEC in THF (Table 2, Run 9). The polymerization of **6** also occurred at 0 °C for 24 h to afford a soluble polymer in 77% yield. Similarly, polymerizations of **7** and **8** with TfOH in CH_2Cl_2 at 30 °C proceeded in heterogeneous states forming white precipitates. After quenching with MeOH, poly(**7**) and poly(**8**), showing good solubility toward common organic solvents such as THF and $CHCl_3$, were obtained in good to quantitative yield. M_n of poly(**6–8**)s produced with TfOH in CH_2Cl_2 was less than 3800 g mol^{-1}, even though the feed molar ratio between monomer and initiator (M/I) was increased. Similarly, Tf_2NH induced ring-opening polymerization of **6** and **8** in CH_2Cl_2 at −78 °C, as observed in the polymerizations of **2–5**. In each case, a white precipitation was immediately observed when we mixed Tf_2NH and monomer in CH_2Cl_2. The M_ns of resultant poly(**6**) and poly(**8**) respectively were 3300 and 5100 g mol^{-1}. The MWDs of polymers obtained with Tf_2NH were broader than



SCHEME 4 Synthesis of **7** and **8**.

TABLE 2 Cationic and Radical Polymerization of **6**, **7**, and **8**[a]

Run	DHA	Initiator	M/I	Solvent	Temperature (°C)	Time (h)	Yield[b] (%)	SEC in THF[c] $M_n \times 10^{-3}$	SEC in THF[c] M_w/M_n	T_{10}[d] (°C)
9	**6**	TfOH	41	CH_2Cl_2	0	24	77	2.2	1.22	437
10	**6**	TfOH	17	CH_2Cl_2	30	24	87	2.2	1.25	438
11	**6**	Tf_2NH	18	CH_2Cl_2	−78	24	76	3.3	1.60	440
12	**7**	TfOH	19	CH_2Cl_2	30	6	35	1.6	1.35	389
13	**7**	TfOH	23	CH_2Cl_2	30	40	68	2.5	1.32	451
14	**8**	TfOH	69	CH_2Cl_2	0	24	40	3.8	1.25	308
15	**8**	TfOH	19	CH_2Cl_2	30	24	77	2.5	1.45	448
16	**8**	Tf_2NH	41	CH_2Cl_2	−78	24	100	5.1	1.92	462
17	**8**	Tf_2NH	76	CH_2Cl_2	−78	24	100	3.7	1.94	466
18[e]	**8**	TfOH	38	*n*-Heptane	0	24	0	–	–	–
19[e]	**8**	TfOH	34	*n*-Heptane	30	24	47	2.4	1.39	388
20[e]	**8**	TfOH	42	*n*-Heptane	30	72	78	6.7 (7.5[f])	1.29 (1.45[f])	449
21[e]	**8**	TfOH	96	*n*-Heptane	30	168	57	5.0	1.59	425
22[e]	**8**	TfOH	38	*n*-Heptane	70	24	100	3.7	1.61	448
23[e]	**8**	Tf_2NH	43	*n*-Heptane	−78	24	84	5.0	1.88	469
24	**6**	AIBN	4.5	BULK	80	24	29	2.0	1.34	319
25	**8**	AIBN	8.2	BULK	80	24	49	2.1	1.63	411

[a] Quenched with MeOH.
[b] MeOH insoluble part.
[c] Calibrated by polystyrene standards.
[d] 10% weight loss temperature by TGA.
[e] 20–30 vol % of CH_2Cl_2 was contained in the polymerization system.
[f] M_n(RALLS) was obtained by RALLS-SEC.

those of polymers formed with TfOH, while the polymerization temperatures of the former ones were much lower than the latter ones.

We subsequently employed *n*-heptane, a nonpolar hydrocarbon, as the solvent for the polymerization of **8**,[19] since poly(**8**) was soluble in hydrocarbons, as described below. When we used TfOH as initiator for the polymerization, no polymerization was observed at 0 °C after 24 h (Run 18). On the other hand, the polymerization of **8** certainly proceeded at higher temperatures (at 30 and 70 °C), and white precipitations slowly formed in the polymerization systems after 24 h. The conversion of **8** was 47% after 24 h at 30 °C, and it reached 78% after 72 h. The SEC trace of the poly(**8**) obtained with TfOH in *n*-heptane after 72 h [Run 20, Fig. 1(B)] was apparently observed at higher molecular weight region compared with that after 24 h [Run 19, Fig. 1(A)].[20] M_w and M_n of the higher molecular weight sample (Run 20) were estimated to be 10,900 and 7540 g mol^{-1} ($M_w/M_n = 1.45$) in the RALLS-SEC measurement in THF.[21] This indicates that ca. 27 adamantane-1,3-diyl units are connected in one polymer chain on average. Since the significant tailing probably due to the terminated oligomers was present in Figure 1(A), the termination and/or the chain transfer reactions might not be negligible, as discussed later. In fact, the conversion and molecular weight did not increase even after the prolonged polymerization time, when the feed molar ratio between monomer and initiator (M/I) was increased (Run 21). Furthermore, although the polymerization was completed within 24 h at 70 °C (Run 22), molecular weight was decreased and MWD was further broadened.

The polymerization of **8** in *n*-heptane was also carried out with Tf_2NH at −78 °C. Even at −78 °C, a white precipitation immediately formed in *n*-heptane, indicating the rapid propagation of **8** with Tf_2NH. Poly(**8**) ($M_n = 5000$ g mol^{-1}) was obtained in 84% yield after 24 h. Probably, the formation of a covalent bond between the adamantane skeleton and Tf_2N group is strongly prohibited by a bulky Tf_2N^- anion and/or a bridgehead 1-adamantyl cation[22] even in *n*-heptane at a very

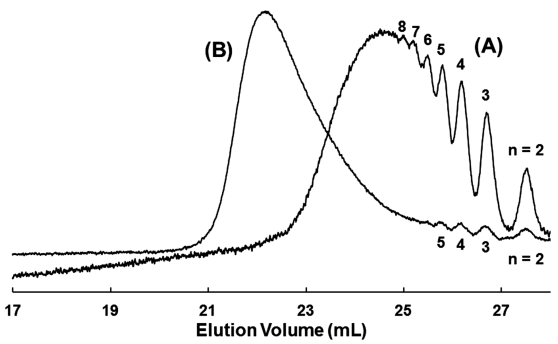


FIGURE 1 SEC traces (THF solvent) of poly(**8**) obtained with TfOH in *n*-heptane at 30 °C: after 24 h, Run 19 (A); after 72 h, Run 20 (B).

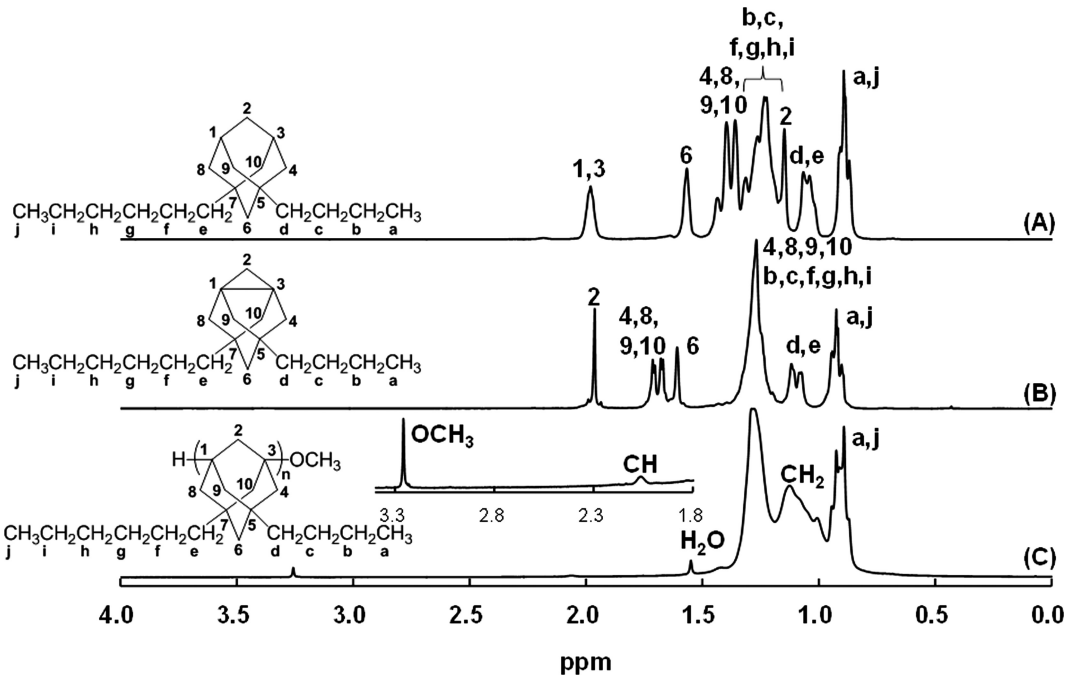


FIGURE 2 ^{1}H NMR spectra of 1-butyl-3-hexyladamantane in $CDCl_3$ (A), **8** in C_6D_6 (B), and poly(**8**) in $CDCl_3$ (C).

low temperature. Then, the polymerization of **8** rapidly proceeds with the naked propagating 1-adamantyl cation derived from **8** and Tf_2NH even at −78 °C in *n*-heptane. Contrary to the polymerization with Tf_2NH, the polymerization of **8** with TfOH is retarded at 0 °C by the formation of a 1-adamantyl triflate, a dormant species of the propagating chain end, in *n*-heptane (Run 18). It is noted that the polymerization of **8** certainly proceeds at 0 °C with TfOH in polar CH_2Cl_2 (Run 14). We now believe that changing of the solvent from polar CH_2Cl_2 to nonpolar *n*-heptane is effective for the formation of poly(**8**) with a higher M_n value to some extent. In nonpolar solvents, ionic dissociation of a propagating species might be suppressed to reduce the frequency of unknown termination and/or chain transfer reactions, as discussed below.

Finally, we performed radical polymerization of **6** and **8** with AIBN in bulk at 80 °C for 24 h. The viscosity of the reaction system increased with the reaction time. After lowering the temperature and quenching with MeOH to convert the residual monomers into corresponding ring-opening products, which are intact toward oxygen,[8,18] white powder of poly(**6**) and poly(**8**) was respectively obtained in 29 and 49% yield by precipitation in MeOH. The M_ns of radically produced polymers were around 2000 g mol^{-1}, as shown in Table 2. NMR measurements confirmed that the chemical structures of the polymers were in good agreement with those obtained by cationic polymerization. These results indicate that the ring-opening polymerization of **6** and **8** also proceeds in radical mechanisms to give corresponding poly(1,3-adamantane)s.

Polymerization Mechanism

The chemical structures of the resulting poly(**4–8**)s were characterized by ^{1}H and ^{13}C NMR spectroscopy to discuss the mechanism of cationic ring-opening polymerization. Both the ^{1}H and ^{13}C NMR spectra of the poly(**4–8**)s showed all the signals expected for the repeating units of poly(1,3-adamantane)s consisting of adamantane-1,3-diyls. Figure 2 shows the ^{1}H NMR spectra of 1-butyl-3-hexyladamantane, **8**, and poly(**8**). After polymerization, the ^{1}H NMR signals of poly(**8**) became broader than those of **8**, and appeared in a limited region between 0.8 and 1.4 ppm. In addition, two characteristic small signals derived from the terminal moieties were observed at 2.1 and 3.3 ppm in the magnified spectrum of poly(**8**). The former corresponds to a methine proton of the adamantane ring at the initiating unit, which derived from the protonation of **8** with TfOH at the initiation step. The resulting 1-adamantyl cation or its triflate induces the successive ring-opening polymerization of **8**. On the other hand, the latter corresponds to a CH_3O proton at the terminal, which is introduced by the nucleophilic termination of MeOH with the propagating 1-adamantyl cation.[23] From the relative intensity of signals, the molecular weight of poly(**8**) (Run 20, $M_n$obsd = 7500 g mol^{-1}) can be estimated to be 3250 (from the methine proton) or 11,300 g mol^{-1} (from the CH_3O proton). In other words, the end-functionality (content of the CH_3O group) is estimated to be 44% by comparing the relative intensity of both end-functionalities. We now speculate that some termination or chain transfer reaction occurs via hydride transfer between the propagating carbocation of poly(**8**) and some protogenic species in the polymerization media, as shown in Scheme 5.[24]

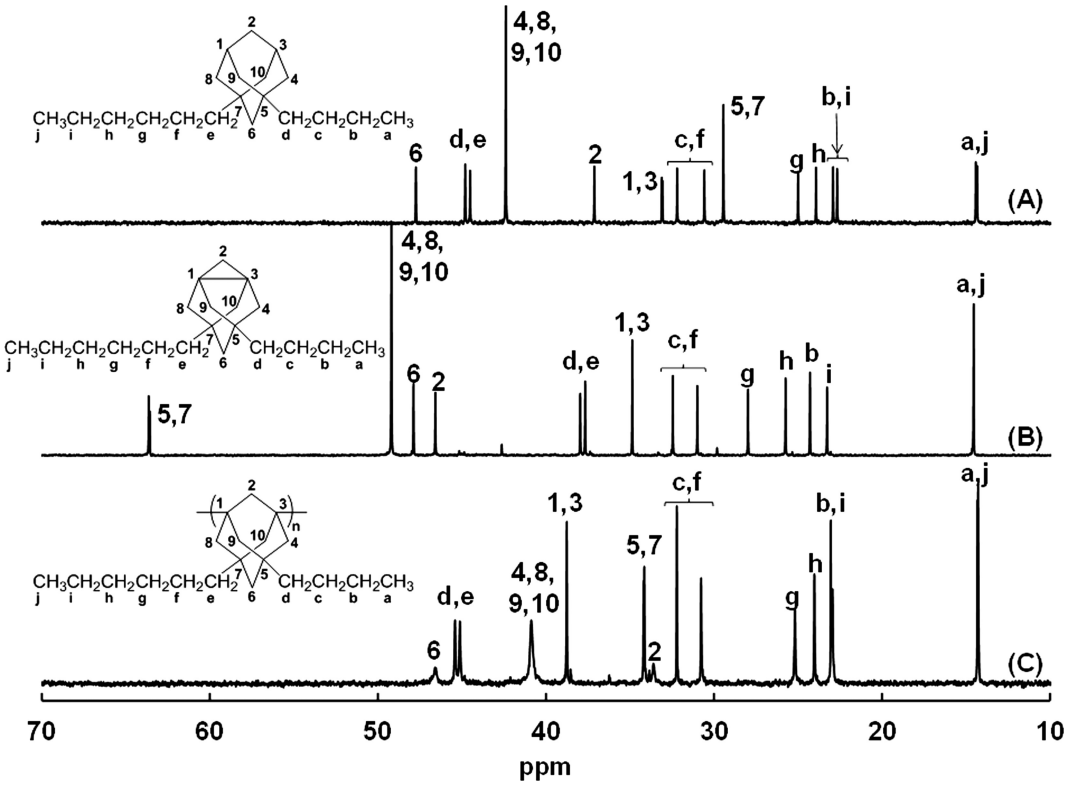


FIGURE 3 ^{13}C NMR spectra of 1-butyl-3-hexyladamantane in $CDCl_3$ (A), **8** in C_6D_6 (B), and poly(**8**) in $CDCl_3$ (C).

This causes the formation of poly(**8**) possessing two methine protons at both terminals (56%) to result in the increase of the relative intensity of the methine proton signal in Figure 2(C), and then the products involve two poly(**8**) series carrying different end-functionalities.[25]

On the other hand, the ^{13}C NMR spectra of 1-butyl-3-hexyladamantane, **8**, and poly(**8**) provide additional information on the repeating units, as shown in Figure 3. In each spectrum, seventeen carbon signals, expected from their molecular symmetries, were observed, while several signals (a and j, 5 and 7, and 4, 8, 9, and 10) almost overlapped. The signals of the adamantane skeletons of **8** drastically shifted from those of 1-butyl-3-hexyladamantane toward the downfield region except for one methylene carbon away from the propellane bond. After the polymerization, most of the signals corresponding to the adamantane skeleton of **8** shifted to the upfield region, where the signals of 1-butyl-3-hexyladamantane are located. These clearly indicate the drastic change of the electronic environment during the ring-opening reaction. The signal of inverted quaternary carbon of **8** at 35 ppm completely disappeared, and a new quaternary carbon signal of the carbon–carbon linkage between adamantane-1,3-diyl units alternatively appeared at 39 ppm after the polymerization. Other ^1H and ^{13}C NMR spectra of poly(**4–7**)s also substantiate that the ring-opening polymerizations of DHAs exclusively occur to give corresponding poly(1,3-adamantane)s carrying various alkyl groups through the breaking of the 1,3-propellane σ-bonds in DHAs (Scheme 1).

Solubility

The solubilities of a series of poly(1,3-adamatnane)s obtained by cationic ring-opening polymerizations are summarized in Table 3. It is demonstrated that the solubility of alkyl-substituted poly(**4–8**)s was higher than that of nonsubstituted poly(**1**). Similar to the case of poly(**2**),[10] we again realized that the introduction of flexible alkyl substituents onto the adamantane ring was effective to induce the solubility of poly(1,3-adamantane)s. In the cases of mono-alkyl-substituted derivatives, poly(**4**) ($M_n = 4100$ g mol^{-1}) possessing the hexyl group showed similar solubility as butyl-substituted poly(**2**) ($M_n = 6900$ g mol^{-1}), indicating the negligible effect of a longer alkyl group on the improvement of solubility. Furthermore, it was difficult to compare the solubility of octyl-substituted poly(**5**) ($M_n = 2800$ g mol^{-1}) with poly(**2**), because the M_n of poly(**5**) was considerably lower than the poly(**2**) sample. On the other hand, the high molecular weight poly(**8**) possessing butyl and hexyl groups in each repeating unit apparently showed excellent solubility toward common organic solvents such as benzene, carbon tetrachloride, chloroform, and THF. Interestingly, poly(**8**) was also soluble even in aliphatic hydrocarbons such as *n*-hexane and cyclohexane, indicating the high affinity of alkyl side chains for nonpolar solvents. In addition, asymmetrical poly(**6**) and poly(**7**) possessing two different alkyl groups exhibited high solubility, similar to poly(**8**), although the effect of molecular weight on the observed solubility cannot be ruled out. We now believe that the introduction of two different alkyl substituents on the repeating units is

TABLE 3 Solubility of Poly(**1**,**3**-adamantane)s

Solvent	Poly(**1**)	Poly(**2**)	Poly(**3**)	Poly(**4**)	Poly(**5**)	Poly(**6**)	Poly(**7**)	Poly(**8**)
M_n (g mol^{-1})	–	6900	–	4100	2800	3300	2500	7500
n-Hexane	I	I	I	I	I	S	PS	S
Cyclohexane	I	I	I	I	S	S	S	S
Benzene	I	I	I	I	I	S	S	S
Toluene	I	I	I	I	I	S	S	S
1,2-Dichlorobenzene	I	S	I	PS	PS	S	S	S
CCl_4	I	I	I	I	S	S	S	S
$CHCl_3$	I	I	I	I	S	PS	S	S
CH_2Cl_2	I	I	I	I	I	PS	I	PS
Acetone	I	I	I	I	I	I	I	I
Diethyl ether	I	I	I	I	I	I	I	I
THF	I	I	I	I	I	PS	I	S
DMF	I	I	I	I	I	I	I	I
MeOH	I	I	I	I	I	I	I	I

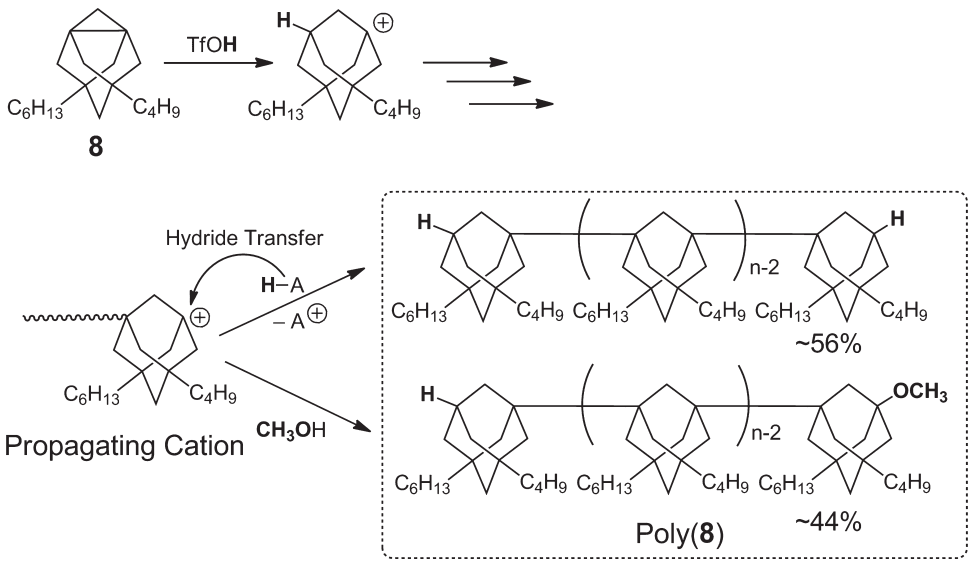
S, soluble; I, insoluble; PS, partially soluble.

significantly effective to attain the enhanced solubility of poly(1,3-adamantane)s by diminishing the symmetry.[12]

It is noteworthy that the solubilities of poly(**6**) and poly(**7**) are higher than the isomeric poly(**3**), although their total carbon numbers of side chains are the same. The difference between these two polymers is the symmetry of the repeating unit structure; poly(**6**) possesses two isomeric butyl substituents and poly(**7**) possesses short (ethyl) and long (hexyl) linear alkyl substituents. In addition, soluble poly(**5**) carrying an octyl group in each unit, $(C_{18}H_{30})_n$, is also an isomer of insoluble poly(**3**). These results undoubtedly prove that the symmetry of the repeating units of poly(1,3-adamantane)s is one of the important factors determining the solubility of polymers.

Thermal Stability

The resultant poly(1,3-adamantane)s showed fairly high thermal stability in thermogravimetric analysis (TGA) measurement. Figure 4 shows the TGA curves of poly(**4**), poly(**5**), poly(**6**), and poly(**8**) obtained by cationic ring-opening polymerization, in addition to that of poly(**2**). All poly(1,3-adamantane)s start to decompose at around 300 °C, and 10% weight loss temperatures (T_{10}) of most samples were over 400 °C, as well as the poly(**2**) previously synthesized.[10] The T_{10} values tended to increase with the molecular weights of poly(1,3-adamantane)s (Tables 1 and 2). The observed high thermal stability is derived from the robust linkages between two adamantane skeletons as well as the bulky and stiff adamantane-1,3-diyl moieties.



SCHEME 5 Plausible polymerization mechanism of **8**.

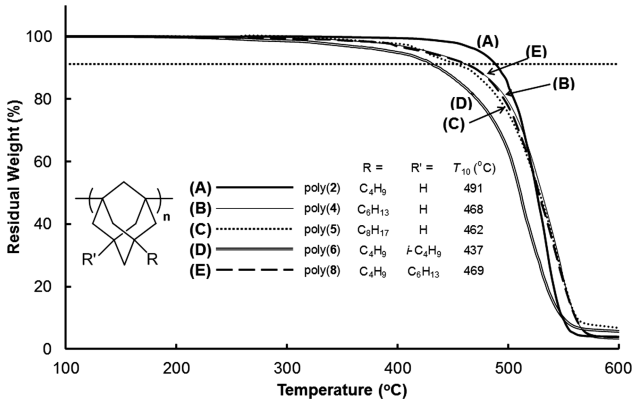


FIGURE 4 TGA curves of poly(1,3-adamantane)s; (A) solid thick line, poly(**2**); (B) solid thin line, poly(**4**); (C) dotted line, poly(**5**); (D) double line, poly(**6**); (E) dashed line, poly(**8**).

We also checked the glass transition temperature (T_g) of polymers by differential scanning calorimetry (DSC) measurement, but no T_g was observed in any polymer before thermal degradation (at least lower than 300 °C). We have reported that only a series of poly(**2**) exhibited T_g, and T_g reached 205 °C in the poly(**2**) sample with the highest M_n (6000 g mol^{-1}).[10] The longer alkyl side chain or further alkyl substitution on the adamantane moiety might restrict the mobility of the polymer main chain of poly(**4–8**)s. It is also noteworthy that no melting point or crystalline behavior of side chains was observed on heating and cooling scans for poly(**4–8**)s, even though long alkyl chains such as octyl substituents were installed. We now consider from the observed DSC traces that all these poly(1,3-adamantane)s are totally amorphous.

CONCLUSIONS

In conclusion, we have succeeded in the synthesis of new types of DHAs possessing various alkyl groups, **4–8**, to expand the range of polymerizable cyclic monomers. The ring-opening polymerizations of these novel [3.3.1]propellane derivatives certainly proceed to afford the corresponding poly(1,3-adamantane)s by breaking the inverted carbon–carbon bonds under cationic and radical conditions similar to our previous reports on **1–3**.[10] The solubilities of poly(**6–8**)s possessing asymmetrical repeating units are significantly enhanced compared with those of nonsubstituted poly(**1**) and symmetrical poly(**3**). The introduction of the flexible linear alkyl groups on the resulting polymers and asymmetrical structure in repeating unit allowed the detailed characterization of poly(1,3-adamantane)s and discussion of the polymerization mechanism because of the sufficient solubility. In particular, poly(**8**) carrying butyl and hexyl substituents is soluble in various organic solvents such as hexane, benzene, chloroform, and THF, and shows high thermal stability (T_{10} = 469 °C).

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18 Similar spontaneous copolymerizations of **1** with oxygen readily occurred by simply exposing of **1** to air to afford a copolymer containing peroxide linkage.[8]

19 20–30vol% of CH_2Cl_2 for the solvent of initiator was contained in the polymerization system.

20 The observation in SEC traces suggests the slow propagation of **8** and the stability of the propagating species, since the most part of SEC trace shifted after 48 h. Similar slow propagation rate and the significant stability of the propagating 1-adamantyl cation have been observed in the polymerization of 2 initiated with TfOH in CH_2Cl_2.[10c]

21 M_n and MWD of poly(**8**) (Run 20) were independently determined to be 8500 g/mol and $M_w/M_n = 1.30$ in the high temperature SEC measurement in ODCB using polystyrene standards. This also supported the molecular weight of poly(**8**) sample.

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23 We already confirmed that the substitution reaction of 1-adamantyl triflate and MeOH proceeded in quantitative efficiency to afford 1-methoxyadamantane.

24 A most probable candidate for protogenic species is a trace amount of adamantane derivatives, which forms during the synthesis of 1,3-dehydroadamantanes by the reduction of the corresponding 1,3-dibromoadamantanes with lithium metal. In fact, the dehydroadamantane monomers contained 1–3% adamantane derivatives after the vacuum distillation. These adamantanes possess methine hydrogens on the tertiary bridgehead carbons.

25 Although we attempted to analyze the structures and end-functionalities of poly(**4**-**8**)s by MALDI-TOF-MS, the clear signal could not be obtained in each case.