Spontaneous Copolymerization of 1,3-Dehydroadamantane

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Summary: Copolymerizations of 1,3-dehydroadamantane, **1**, and various vinyl monomers were carried out in THF at room temperature. On mixing of **1** with electron-deficient vinyl monomers such as acrylonitrile and methyl acrylate in the absence of initiator, the copolymerization spontaneously proceeded to give alternating copolymers in 28–88% yields. By contrast, no reaction of **1** occurred at all, when isobutyl vinyl ether or styrene was mixed under the similar conditions. These results indicate the high electron density of a central σ-bond in a strained [3.3.1]propellane derivative, **1**. Alternating sequences of the resulting copolymers were characterized by NMR and MALDI-TOF-MS measurements. DSC and TGA measurements revealed the high thermal stability of the alternating copolymers containing bulky, stiff, and strain-free adamantane skeletons.

Keywords: 1,3-dehydroadamantane; adamantane; alternating copolymer; electron-deficient monomers; spontaneous copolymerization

Introduction

Small ring propellanes such as [1.1.1]-, [2.2.2]-, and [2.2.1]propellanes are very unique molecules,[1] since the highly reactive σ-bonds between the bridgehead carbons with inverted tetrahedral geometry readily react with various substrates to give the ring-opening products. Since they are considered as the cyclic monomers, anionic[2] and radical[3] ring-opening polymerizations of [1.1.1] propellane derivatives have been investigated to afford poly(propellane)s. Interestingly, the spontaneous copolymerization of [1.1.1]propellanes and electron-deficient monomers gave alternating copolymers.[4]

1,3-Dehydroadmantane,[5]**1**, is a typical [3.3.1]propellane derivative showing high reactivity towards free-radical and electrophilic ring-opening reactions with oxygen, bromine, and acetic acid to produce 1,3-disubstituted adamantanes. We have recently succeeded in the cationic and free-radical ring-opening polymerizations of **1** and 5-butyl-1,3-dehydroadamantane (**2**) via breaking of 1,3-propellane linkage to afford the poly(1,3-adamantane)s showing high thermal stability.[6] Although [1.1.1] propellanes also undergo the ring-opening polymerization, the polymerizabilities of **1** and **2** largely differ from that of [1.1.1]propellane. For example, the anionic polymerization of [1.1.1]propellanes smoothly proceeded,[2] but no reaction of **1** and **2** occurred with the strong nucleophiles such as *n*-BuLi and Grignard reagent. This clearly shows much higher electron densities of bridgehead C–C bonds in **1** and **2** compared to the [1.1.1] propellanes. We herein report the spontaneous crossover reaction between **1** and electron-deficient vinyl monomers such as acrylonitrile (AN) and methyl acrylate (MA), leading to novel alternating copolymers containing bulky and stiff adamantane (Ad) moieties, as shown in Scheme 1.[7]

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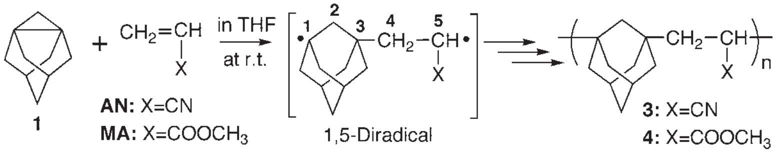

Scheme 1.

Results and Discussions

The reaction of 1,3-dibromoadamantane with lithium in THF gave **1** in 81% yield. Although **1** was stable in a sealed tube in C_6D_6 at least for two years, it easily reacted with oxygen to give a copolymeric peroxide having C–O–O–C linkage.[5] Therefore, we carefully treated **1** under argon and carried out the polymerization in an all-glass apparatus under high vacuum conditions using break-seal technique.

The reaction of **1** with one equivalent of various vinyl monomers showing different polymerizability was performed in THF at room temperature for 24 h, as shown in Table 1. When we employed isobutyl vinyl ether (IBVE) or styrene (St) as a comonomer, no reaction occurred with **1** at all to result in a quantitative recovery of the starting comonomers. By contrast, **1** underwent the spontaneous copolymerizations with the polar monomers such as AN and MA to give the corresponding copolymers, **3** and **4**, in 28–88% yields under the identical conditions. The copolymerization proceeded homogeneously and in the absence of initiator. Polymerizations were terminated with acetic acid, and the polymer was obtained by precipitating of the reaction mixture into methanol.[8] In contrast to homopolymers of **1**[6,9] and AN, the resulting copolymers were soluble in various organic solvents including chloroform and THF, indicating that the structure of copolymer is quite different from both the homopolymers. The composition of copolymer was determined by elemental analysis for **3** and by ^{1}H NMR measurement for **4**, respectively. The molecular weights of copolymers were analyzed by the RALLS-SEC measurement with RI, LS, and viscosity detectors in THF, and the M_n values were ranging from 6000 to 23,000. The SEC curves of **3** and **4** were unimodal, and the M_w/M_n values were 1.6–2.9.

The results of copolymerization of **1** are summarized in Table 1. When we mixed **1**

Table 1.
Copolymerization of **1** with M2 Comonomers in THF at room temperature.a)

run	M2	$[\mathbf{1}]_0$ b)	time	yield	Ad content c)	$10^{-3}M_n$ d)	M_w/M_n d)	T_g e)
		mol%	h	%	mol%			°C
1	IBVE	45	24	0	–	–	–	–
2	St	49	24	0	–	–	–	–
3	AN	15	24	52	35	6.0	2.26	161
4	AN	51	0.5	28	49	23	1.58	231
5	AN	51	3	58	49	17	2.01	226
6	AN	51	8	62	49	9.4	2.38	226
7	AN	51	24	62	49	8.8	2.40	222
8	AN	80	24	30	51	18	2.90	217
9	MA	17	24	88	28	8.0	2.20	86
10	MA	48	24	58	40	9.4	1.66	129
11	MA	77	24	34	49	9.0	2.60	143

a) Carried out under high vacuum conditions (10^{-6} mmHg);
b) Initial mol% of **1** in the reaction mixture;
c) Ad content in the resulting copolymer estimated by elemental analysis (runs 3–8) or ^{1}H NMR (runs 9–11);
d) Estimated by RALLS-SEC measurement;
e) Measured by DSC.

and AN at 1:1 molar ratio (runs 4–7) in THF, the yield of copolymer increased with polymerization time and reached ca. 60% after 8 h. No apparent copolymerization further proceeded after 24 h. The Ad content in each copolymer was constant and almost 50%. When the reaction of **1** with AN was carried out with a molar ratio of 15/85 (run 3), the copolymer with 35% Ad unit was obtained in 52% yield.[10] This means that most of **1** is incorporated with AN to form the copolymer. On the other hand, even when four-fold **1** was reacted with AN (run 8), the resulting copolymer was composed of only 51 mol% of Ad moiety. When we employed MA as a comonomer, the similar copolymerization behavior was observed. These results clearly indicate the lower homopolymerizability of **1** compared with AN and MA. The observed polymerization behavior suggests that the resulting copolymers have strongly alternating tendency, when excess amount of comonomer to **1** was charged in the reaction system. We then characterized the chemical structure of the resulting copolymers containing 50 mol% Ad units, by ^{1}H and ^{13}C NMR spectroscopies in conjunction with MALDI-TOF-MS.

The ^{1}H and ^{13}C NMR spectra of **3** and **4** were completely different from those of 1,1-biadamantane[11] and poly(AN) or poly(MA), indicating the lack of homosequences and the highly alternating sequence. For example, the ^{13}C NMR spectrum of **3** is shown in Figure 1. In the aliphatic region between 28 and 45 ppm, it reveals the set of nine signal groups expected for the repeating unit of alternating copolymer **3** along with the sharp nitrile signal at 122.2 ppm. All the signals are successfully assigned by the ^{1}H-^{1}H, ^{1}H-^{13}C, and DEPT pulse sequences and by comparison with several authentic compounds such as 1,3-dimethyladamantane and 1,3-dibutyladamantane.[9] Only the central 1,3-linkage of **1** should be exclusively opened to participate in the polymerization, since two sharp signals assigned to the quaternary carbons of Ad ring in the main chain are observed at 33.5 and 36.0 ppm. This simple spectrum indicates not only the alternating sequence but also the highly regulated head-to-tail linkage of **3**. Nevertheless, splitting of several methylene carbons on Ad skeleton took place probably due to the two diads, syn and anti, derived from newly-formed centers of asymmetry along with the main chain.

The MALDI-TOF-MS of **3** also supported the chemical structure of alternating copolymer derived from **1** and AN. Three series of signals with the intervals of 187.28 Da were observed between 1000 and 5000 mass/charge region. This strongly indicated that three series of copolymers having the

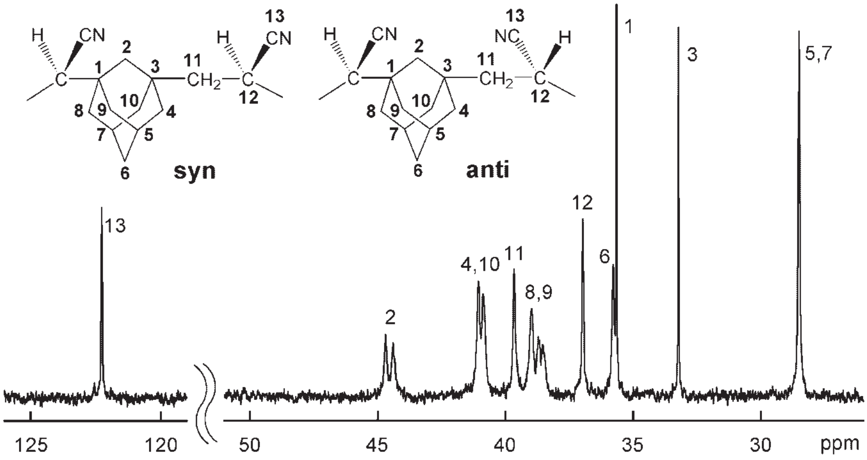

Figure 1.
^{13}C NMR Spectrum of **3** in $CDCl_3$.

same repeating units were included, and the observed intervals were corresponding to a total mass (187.28 Da) of **1** and AN. If the strongest series of signals contain the same number of comonomer units, other two minor series of signals are corresponding to the copolymers containing one more **1** unit and one more AN unit. Thus, the MALDI-TOF-MS analysis is a strong tool to prove the chain-growth process of spontaneous copolymerization not the step-growth process.

The glass transition temperatures (T_g) of copolymers were measured by DSC. The T_g values increased with the content of Ad skeleton and M_n value of the copolymers. The T_gs of **3** and **4** with ca. 50% Ad contents were 231 °C and 143 °C, respectively. These values were ca. 130 °C higher than those of poly(AN) ($T_g = 95\,^\circ C$) and poly(MA) ($T_g = 10\,^\circ C$). TGA analysis of **3** and **4** showed 10% weight loss at 451 and 467 °C under nitrogen, respectively. These were much higher than those of homopolymers of AN ($T_{10} = 296\,^\circ C$) and MA ($T_{10} = 340\,^\circ C$).[12]

In conclusion, [3.3.1]propellane **1** is newly proved to be a versatile cyclic monomer to produce novel alternating copolymers containing bulky, strain-free, and thermally-stable adamantane-1,3-diyl moieties on mixing with the polar monomers such as AN or MA. The preliminary experiment in the presence of chain transfer reagents such as carbon tetrabromide and diphenyl disulfide suggests that a 1,5-diradical species (Scheme 1) is a plausible intermediate formed at the initial stage of spontaneous copolymerization.[13] The following highly selective cross-propagation between **1** and electron-deficient monomers might successively proceed to form the corresponding alternating copolymers.

Experimental Part

Materials

Commercially available 1,3-dibromoadamantane and lithium were used without further purification. THF was refluxed over sodium wire for 3 h and distilled from $LiAlH_4$ under nitrogen. AN and MA were purified by vacuum distillation from CaH_2 and diluted with dry THF.

Synthesis of 1

In a two-necked flask, 1,3-dibromoadamantane (17.1 g, 68.5 mmol) was dissolved in dry THF (50 mL) under argon. Lithium wire (1.70 g, 245 mmol) cut in pieces was added to the flask and the reaction mixture was stirred for 24 h at room temperature. After the reaction was completed, the solution was transferred into 100 mL round bottom flask equipped with break-seals. The solution was degassed via three freeze-pump-thaw cycles, and the apparatus was sealed off under high vacuum conditions. The solution was distilled twice to give a THF solution of **1** (0.800 M, 7.15 g, 53.3 mmol, 81%) on a vacuum line into ampules fitted with break-seals in order to remove inorganic residue. The THF solution of **1** was divided into several ampules fitted with break-seal, and the ampules were stored at −30 °C prior to the polymerization.

Polymerization Procedure

All polymerizations were carried out in an all glass-apparatus equipped with break-seals under high vacuum conditions. The following is a typical polymerization procedure. A THF solution (13.8 mL) of **1** (0.477 M, 6.58 mmol, 0.88 g) was mixed with a THF solution (5.15 mL) of AN (1.04 M, 5.36 mmol, 0.28 g) at room temperature. The polymerization proceeded homogeneously. After stirring for 24 h at room temperature, the copolymerization was terminated with acetic acid. The copolymer was precipitated by pouring the polymerization mixture into methanol, and the precipitated polymer was collected by filtration. The copolymer **3** (0.83 g, 72% yield) was obtained by reprecipitation from THF into methanol in order to remove the residual low molecular weight compounds completely. The polymerization of **1** with MA was similarly carried out to afford copolymer **4** in THF at room temperature. The resulting polymer was characterized by

^{1}H and ^{13}C NMR, IR, elemental analysis, and RALLS-SEC measurements.

Selected Data for 3

^{1}H NMR (CDCl$_3$, 300 MHz): 1.2–1.7 (m, CH$_2$), 2.15 (s, CH). ^{13}C NMR (CDCl$_3$, 75 MHz): 28.5 (C-5,7), 33.2 (C-3), 35.6 (C-1), 35.8 (C-6), 37.0 (C-12), 38.5–39.0 (C-8,9), 39.6 (C-11), 40.8–41.0 (C-4,10), 44.4–45.0 (C-2), 122.2 (C-13). IR(KBr): 2904, 2849, 2234 (CN), 1449, 1345 cm^{-1}. Anal. calcd for alternating copolymer $(C_{13}H_{17}N)_n$: C, 83.37%; H, 9.15%; N, 7.48%: found: C, 81.13%; H, 8.96%; N, 7.81%.

Selected Data for 4

^{1}H NMR (CDCl$_3$, 300 MHz): 0.9–1.7 (m, CH$_2$), 2.0 (s, CH), 3.7 (OCH$_3$). ^{13}C NMR (CDCl$_3$, 75 MHz): 28.9 (C-5,7), 33.1 (C-3), 35.9 (C-1), 36.3 (C-6), 39.2, 39.8, 40. 3, 40.8, 41.4 (C-4,8,9,10,11), 44.4–44.6 (C-2), 50.3 (C-12), 51.09 (C14), 176.4 (C-13). IR(KBr): 2903, 2846, 1734 (C=O), 1449, 1158 cm^{-1}.

Measurements

^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX300 (300 MHz for ^{1}H and 75 MHz for ^{13}C) in CDCl$_3$ solution at 25 °C. The chemical shifts were reported in ppm downfield relative to CHCl$_3$ (δ 7.26) for ^{1}H NMR and CDCl$_3$ (δ 77.1) for ^{13}C NMR as standard. Infrared spectra (KBr or NaCl disk) were recorded on a JASCO FT-IR spectrometer. The M_n and molecular weight distribution of copolymers were determined by right angle laser light scattering size exclusion chromatography (RALLS-SEC) using an Asahi Techneion Viscotek Model 302 TDA equipped with three polystyrene gel columns (TOSOH TSKgel GMH$_{HR}$-H X 2 and TSKgel G2000H$_{HR}$) with triple detectors (RI, LS, and viscosity). THF was an eluent at 30 °C at a flow rate of 1.0 mL·min^{-1}. The T_g of polymer was measured by DSC using a Seiko Instrument DSC6220 apparatus under nitrogen at a rate of 10 °C·min^{-1}. A Seiko Instrument TG/DTA6200 was used for TGA analysis at 30–600 °C under nitrogen flow with heating rate of 10 °C· min^{-1}. MALDI-TOF-MS was performed on an AXIMA-CFR (Shimadzu/Kratos) equipped with a 337 nm N$_2$ laser in the linear mode and 20 kV acceleration voltage. 2,5-Dihydroxybenzoic acid (Tokyo Kasei, 97%) was used as matrix, and no ionization reagent was added.

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