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Formation of Alternating Copolymers via Spontaneous Copolymerization of 1,3-Dehydroadamantane with Electron-Deficient Vinyl Monomers

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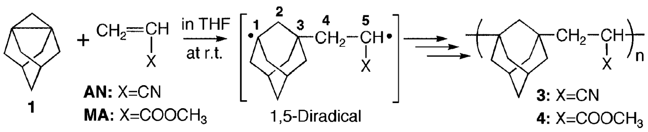
Highly strained small ring propellanes, such as [1.1.1]-,[1] [2.2.2]-,[2] and [2.2.1]propellanes,[3] readily afford the ring-opening products with various substrates[4] since the σ-bonds between the bridgehead carbons with inverted tetrahedral geometry are highly reactive. However, study of the ring-opening polymerization of propellanes has been very limited probably due to their low stability[1−4] and synthetic difficulty.[5] Only anionic[6] and radical[7] ring-opening polymerizations of [1.1.1]propellane derivatives were investigated to afford poly(propellane)s. Interestingly, the spontaneous copolymerization of [1.1.1]propellanes and electron-deficient monomers proceeded to give alternating copolymers.[8]

1,3-Dehydroadamantane,[4,9] **1**, is a typical [3.3.1]propellane derivative showing high reactivity toward free-radical and electrophilic ring-opening reactions with oxygen, bromine, and acetic acid to produce 1,3-disubstituted adamantanes. Recently, we have first demonstrated that the cationic and free-radical ring-opening polymerization of **1** or 5-butyl-1,3-dehydroadamantane (**2**) proceeds via breaking of the 1,3-propellane linkage to afford the poly(1,3-adamantane)s showing high thermal stability.[10] Interestingly, the polymerizabilities of **1** and **2** largely differ from those of [1.1.1]-propellanes under the various reaction conditions. For example, the [1.1.1]propellanes readily undergo the anionic polymerization,[6] but no reaction of **1** and **2** occurred with strong nucleophiles, such as *n*-BuLi and Grignard reagent. These findings clearly show much higher electron densities of bridgehead C−C bonds in **1** and **2** compared to those in the [1.1.1]propellanes. Herein, we newly 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.

Scheme 1



Monomer **1** was synthesized in 81% yield by the reaction of 1,3-dibromoadamantane with lithium in THF.[10] Although **1** was stable in a sealed tube in C_6D_6 at least for 2 years, it spontaneously reacted with oxygen to give a copolymeric product having C−O−O−C linkage.[9] We therefore treated **1** under argon and carried out the polymerization in an all-glass apparatus under high vacuum conditions using break-seal technique.

We attempted to react **1** with 1 equiv of various vinyl monomers showing different polymerizability, as shown in Table 1. The reaction was performed in THF at room temperature for 24 h. In the cases of isobutyl vinyl ether (IBVE) and styrene (St), no reaction occurred with **1** at all to result in a quantitative recovery of the starting comonomers. In contrast, the monomers having electron-withdrawing groups, AN and MA, underwent the spontaneous copolymerizations with **1** to give the corresponding copolymers, **3** and **4**, in 28−88% yield under identical conditions. The copolymerization proceeded homogeneously and in the absence of initiator. After termination with acetic acid,[11] the polymer was obtained by precipitating the reaction mixture into methanol. In contrast to homopolymers of **1**[10,12] and AN, the resulting copolymers were soluble in various organic solvents, including chloroform and THF, indicating that the structure of the copolymer is quite different from those of both homopolymers. The composition of the copolymer was measured by elemental analysis for **3** and by ^{1}H NMR for **4**, respectively. The molecular weights of the copolymers were determined by the RALLS−SEC measurement with RI, LS, and viscosity detectors in THF, and the M_n values ranged 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.

Table 1. Copolymerization of **1** with Comonomers in THF at Room Temperature

run	comonomer	[**1**]$_0$^{a} mol %	time h	yield %	content^b mol %	10^{-3} M_n^{c}	T_g^{d} °C
1	IBVE	45	24	0			
2	St	49	24	0			
3	AN	15	24	52	35	6.0	161
4	AN	51	0.5	28	49	23	231
5	AN	51	3	58	49	17	226
6	AN	51	8	62	49	9.4	226
7	AN	51	24	62	49	8.8	222
8	AN	80	24	30	51	18	217
9	MA	17	24	88	28	8.0	86
10	MA	48	24	58	40	9.4	129
11	MA	77	24	34	49	9.0	143

[a] Initial mol % of **1** in the reaction mixture. [b] Ad content in the resulting copolymer measured by elemental analysis (runs 3−8) or ^{1}H NMR (runs 9−11). [c] Estimated by RALLS−SEC measurement. [d] Measured by DSC.

Table 1 summarizes the result of copolymerization of **1**. When we mixed **1** and AN at 1:1 molar ratio (runs 4−7), the yield of the copolymer increased with polymerization time and reached ca. 60% after 8 h. No apparent copolymerization further proceeded even after 24 h. Interestingly, 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.[13] This means that most of **1** is incorporated with AN to form the copolymer. On the other hand, even when 4-fold **1** was reacted with AN (run 8), the resulting copolymer was composed of only 51 mol % of the Ad moiety. Using MA as a comonomer, similar copolymerization behavior was observed. These results clearly indicate the lower homopolymerizability of **1** compared with that of AN and MA. The observed polymerization behavior suggests that the resulting copolymers have strongly alternating tendency. Then, we thoroughly characterized the chemical structure of the resulting copolymers containing 50

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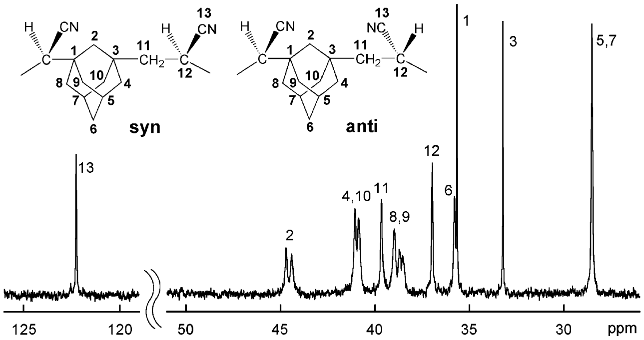

Figure 1. ^{13}C NMR spectra of **3** (run 8) in $CDCl_3$.

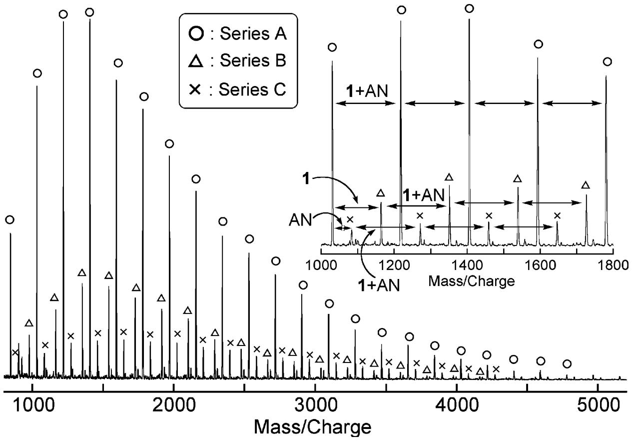

Figure 2. MALDI-TOF-MS of **3** (run 8).

mol % of 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[14] and poly(AN) or poly(MA), indicating the highly alternating sequence and the lack of homosequences. Figure 1 shows the ^{13}C NMR spectrum of **3**. 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 can be 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.[12] Since two sharp signals assigned to the quaternary carbons of the Ad ring in the main chain are observed at 33.5 and 36.0 ppm, only the central 1,3-linkage of **1** should be exclusively opened to participate in the polymerization. The simplicity of the spectrum indicates not only the alternating sequence but also the highly regulated head-to-tail linkage of **3**. Nevertheless, several methylene carbons on the Ad skeleton are split 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 supports the chemical structure of an alternating copolymer derived from **1** and AN, as shown in Figure 2. Three series of signals (A, B, and C) with the intervals of 187.28 Da are clearly observed between 1000 and 5000 mass/charge region.[15] This strongly shows that there are three series of copolymers having the same repeating units, and the observed intervals are corresponding to a total mass (187.28 Da) of **1** and AN. If the strongest series of signals (series A) contain the same number of comonomer units, the other two minor series of signals are corresponding to the copolymers containing one more **1** unit for series B and one more AN unit for series C. To our best knowledge, this MALDI-TOF-MS analysis is the first experimental evidence to prove the chain-growth process of spontaneous copolymerization not the step-growth process.

The glass transition temperatures (T_g) of copolymers measured by DSC increased with the content of Ad skeleton and M_n value of the copolymers. The T_g values of **3** and **4** were 231 and 143 °C, respectively. These observed values were ca. 130 °C higher than those of poly(AN) ($T_g = 95$ °C) and poly(MA) ($T_g = 10$ °C).[16] 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 ($T_{10} = 296$ °C) and MA ($T_{10} = 340$ °C).[16]

In conclusion, [3.3.1]propellane **1** is newly proved to be a versatile 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 a chain transfer reagent suggests that a 1,5-diradical species (Scheme 1) is a plausible intermediate formed at the initial stage of spontaneous copolymerization.[17] The following highly selective cross propagation between **1** and electron-deficient monomers might successively proceed to form the corresponding alternating copolymers.

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Supporting Information Available: Experimental procedures and characterization data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) It was very difficult to analyze the MALDI-TOF-MS of **3** and **4** presumably due to their low ionization tendency. In fact, Figure 2 only shows the low molecular weight fractions of copolymer **3** (run 8). We consider that three series of copolymers possess the same terminal structures with ca. 95 Da, which is almost consistent with a total mass of sodium and THF, although the terminal structures of copolymers have not been identified yet.
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