

## Spontaneous Copolymerization of 1,3-Dehydroadamantanes

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### Introduction

1,3-Dehydroadamantane,<sup>1</sup> **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 demonstrated that the cationic and free-radical ring-opening polymerization of **1** or 5-butyl-1,3-dehydroadamantane (**2**) proceeds via breaking of 1,3-propellane  $\sigma$ -linkage to afford the poly(1,3-adamantane)s showing high thermal stability.<sup>2</sup> By contrast, no reaction occurred with *n*-BuLi or Grignard reagents, indicating a very high electron density of bridgehead C-C bond in **1** and **2**. These contrastive results prompt us to investigate the reactivity of **1** in more detail. 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.<sup>3</sup>

#### Scheme 1.

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### Results and discussion

We initially attempted to react **1** with one equivalent 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 bearing electron-withdrawing groups, AN and MA, underwent the spontaneous copolymerizations with **1** in the absence of any initiator to give the corresponding copolymers, **3** and **4**, in 28-88% yield under the identical conditions. After termination with acetic acid, the polymer was obtained by precipitating of the reaction mixture into methanol. The resulting copolymers were soluble in various organic solvents including chloroform and THF in contrast to the homopolymers of **1** and AN. The composition of copolymer was estimated from either elemental analysis for **3** or from <sup>1</sup>H NMR for **4**. The molecular weights of copolymers were determined 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. When we reacted 1:1 mixture of **1** and AN (runs 4-7), the yield of 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%, while the  $M_n$  values significantly decreased as the conversion increased. 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. This means that most of **1** is consumed and 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 for **1**, the similar copolymerization behavior was observed. 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 mol% Ad units, by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopies in conjunction with MALDI-TOF-MS.

The <sup>1</sup>H and <sup>13</sup>C NMR spectra of **3** and **4** were completely different from those of 1,1-biadamantane and poly(AN) or poly(MA),

indicating the highly alternating sequence and the lack of homosequences. Figure 1 shows the <sup>13</sup>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 <sup>1</sup>H-<sup>1</sup>H, <sup>1</sup>H-<sup>13</sup>C, and DEPT pulse sequences and by comparison with several authentic compounds such as 1,3-dimethyladamantane and 1,3-dibutyladamantane. 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, only the central 1,3-linkage of **1** should be exclusively opened during the polymerization. The simplicity of 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 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  $T_g$  of **3** and **4** reached 231 °C 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). 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).

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

Table 1. Copolymerization of **1** with M2 Comonomers in THF at r.t.

run	M2	[ <b>1</b> ] <sub>0</sub> <sup>a</sup>		time	yield	cont. <sup>b</sup>	10 <sup>-3</sup> M <sub>n</sub> <sup>c</sup>	T <sub>g</sub> <sup>d</sup>
		mol%	h					
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	

<sup>a</sup> Initial mol% of **1** in the reaction mixture. <sup>b</sup> Ad content in the resulting copolymer estimated by elemental analysis (runs 3-8) or <sup>1</sup>H NMR (runs 9-11). <sup>c</sup> Estimated by RALLS-SEC measurement. <sup>d</sup> Measured by DSC.

Figure 1. <sup>13</sup>C NMR Spectrum of **3** in CDCl<sub>3</sub>.

### References

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