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Synthesis of Well-Defined Poly(ethylene-*alt*-1-vinyladamantane) via Living Anionic Polymerization of 2-(1-Adamantyl)-1,3-butadiene, Followed by Hydrogenation

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ABSTRACT: Anionic polymerization of 2-(1-adamantyl)-1,3-butadiene (**1**) was carried out either with *s*-BuLi in cyclohexane at 40 °C or with potassium naphthalenide in THF at −78 °C. The polymerizations of **1** quantitatively proceeded to afford the polymers possessing the predicted molecular weights based on the molar ratios between monomers and initiators and the narrow molecular weight distributions. The microstructure of the resulting poly(**1**) was affected by the initiators and the solvents. The contents of 1,4-repeating unit in poly(**1**)s obtained with *s*-BuLi in cyclohexane and with potassium naphthalenide in THF were 96 and 55%, respectively. The 1,4-rich poly(**1**) was completely converted into a novel saturated alternating copolymer, poly(ethylene-*alt*-1-vinyladamantane) (P(E-*alt*-VAd)), by the hydrogenation with *p*-toluenesulfonhydrazide. Poly(**1**) possessing the M_n value over 5000 was hardly soluble in common organic solvents, while the hydrogenated P(E-*alt*-VAd) was soluble in a wide variety of organic solvents. Novel well-defined block copolymers were anionically synthesized by the sequential copolymerization of **1** and styrene. The results of block copolymerization also demonstrated the living property of the propagating chain end of poly(**1**). The resulting poly(**1**) and P(E-*alt*-VAd) started to decompose from 280 and 380 °C in the TGA analyses, respectively. Poly(**1**) and P(E-*alt*-VAd) showed T_gs at 100 and 125 °C on the DSC thermograms.

Introduction

Controls on the thermal property of the polymers have always attracted a great attention to design the novel functional materials. In particular, the incorporations of bulky and rigid alicyclic substituents in the main chain or in the side chain are usually very effective to increase the glass transition temperature (T_g) of various parent polymers.[1−5] Among the substituents, adamantyl skeleton has been proved to induce the drastic enhancement of T_g values as well as the retardation of thermal degradation.[1,3−5] In fact, a number of polymers containing adamantyl skeletons in the main chains and in the side chains have been synthesized via the stepwise[3] and chain polymerizations.[4,5] As a typical example of main chain type polymer, we have synthesized a poly(1,3-adamantane) via the ring-opening polymerization of a highly strained [3.3.1]propellane derivative, 1,3-dehydroadamantane.[6] Furthermore, 1,3-dehydroadamantane undergoes the spontaneous copolymerization with electron-deficient monomers such as acrylonitrile and methyl acrylate without any initiator to form the alternating copolymers containing adamantyl skeleton in the main chain.[7] As a simple example of side chain type polymer, Mathias and co-workers have reported the synthesis of homopolymer and copolymer of 3-(1-adamantyl)propene via the metallocene-catalyzed polymerization to form the all aliphatic polymers containing adamantyl skeletons.[5] They demonstrated that the bulky adamantylmethyl group significantly influenced the T_gs of the copolymers in comparison with the corresponding homopolymers.

We have recently succeeded in the living anionic polymerizations of methacrylates[8] and styrenes[9,10] carrying 1-adamantyl and 3-(1,1′-biadamantyl) moieties to afford the well-defined homopolymers and block copolymers. The resulting polymers possessed the predicted number-average molecular weights (M_ns) based on the molar ratios between monomers and initiators and the narrow molecular weight distributions (MWDs). In addition, they exhibited markedly high T_g values and enhanced thermal stabilities derived from the adamantyl substituents in each monomer unit. In the cases of random copolymers, the T_g values were readily tunable by changing the feed molar ratio of comonomers. Furthermore, the living nature of the polymerization enabled to produce a novel thermoplastic elastomer showing high service temperature via the sequential copolymerization of 4-(1-adamantyl)styrene and isoprene.[10]

It is well-known that 1,3-dienes such as 1,3-butadiene and isoprene are also the representative monomers capable of the living anionic polymerization as well as styrenes and methacrylates.[11] Under the suitable conditions, the anionic polymerizations of 1,3-dienes afford the well-defined polymers having controlled M_ns and narrow MWDs with regulated microstructures, and the living character of the polymerization allows us to synthesize the various block copolymers and the chain-end-functionalized polymers. In this study, we newly design and anionically polymerize a 1,3-diene derivative, 2-(1-adamantyl)-1,3-butadiene (**1**), and also attempt to synthesize a novel alternating hydrocarbon copolymer, poly(ethylene-*alt*-1-vinyladamantane) (P(E-*alt*-VAd)), via the subsequent hydrogenation of the resulting poly(**1**) with predominant 1,4-repeating unit as shown in Scheme 1. Although **1** has been already synthesized and employed in the Diels−Alder reactions,[12] no attempt of the polymerization has been reported. Bulky and rigid adamantyl side chain on the 1,3-butadiene framework will strongly affect the polymerization behaviors such as rate of polymerization and microstructures of the resulting polydiene. Furthermore, drastic substituent effects on thermal properties for the resulting poly(**1**)

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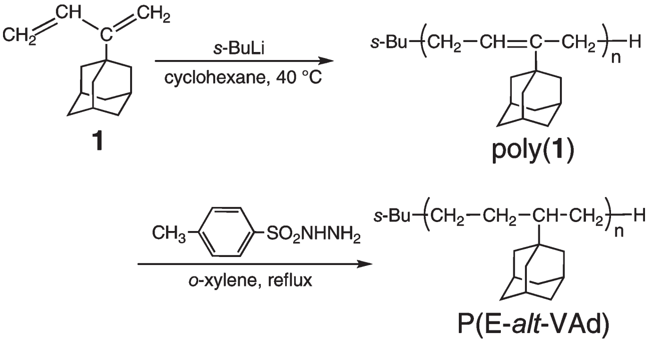
Table 1. Anionic Polymerization of 1

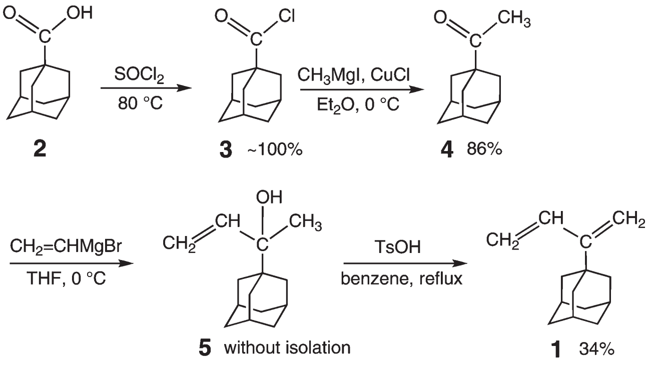
							M_n (kg/mol)			
run	solvent	temp (°C)	initiator (mmol)	monomer (mmol)	time (h)	yield (%)	calcd[a]	RALLS[b,c]	NMR[d]	M_w/M_n[c,e]
1	cyclohexane	40	*s*-BuLi, 0.316	3.42	3	100	2.0	2.3[f]	2.1[f]	1.08[f]
2	cyclohexane	40	*s*-BuLi, 0.144	3.92	3	100	5.1	6.0		1.09
3	cyclohexane	40	*s*-BuLi, 0.0586	3.21	3	100	10	11		1.31
4	cyclohexane	40	*s*-BuLi, 0.0651	6.47	3	100	19	21		1.38
5	*n*-heptane	40	*s*-BuLi, 0.381	4.96	3	100	2.4	3.1	2.5	1.08
6	*n*-heptane	40	*s*-BuLi, 0.103	3.22	3	100	5.9	6.5		1.17
7	*n*-heptane	40	*s*-BuLi, 0.273	14.1	5	100	9.7	10		1.32
8[g]	THF	−78	*s*-BuLi, 0.0880	3.72	24	0	0			
9	THF	−30	*s*-BuLi, 0.275	3.14	72	100	2.1	2.4[f]	2.4[f]	1.07[f]
10[h]	THF	−78	K-Naph[i], 0.127	3.38	3	8	2.8	[j]		[j]
11	THF	−78	K-Naph, 0.466	3.00	24	100	2.4	4.3[f]		1.12[f]
12	THF	−78	K-Naph, 0.110	3.20	24	100	11	16		1.08

[a] M_n(calcd) = (MW of monomer) × [monomer]/[initiator] × yield + MW of initiator residue. [b] M_n(RALLS) was obtained by RALLS-SEC using THF as an eluent at 30 °C. [c] Data after hydrogenation. [d] M_n(NMR) was determined by the end-group analysis using ^{1}H NMR. [e] M_w/M_n was obtained by SEC calibration using polystyrene standards in THF. [f] Data before hydrogenation. [g] Conversion = 0%. [h] Conversion = 28%. [i] Potassium naphthalenide. [j] No data due to the low yield of polymer.

Scheme 1. Anionic Polymerization of 1 and Hydrogenation of Poly(1)



Scheme 2. Synthesis of 1



will be expected, since the adamantyl group is directly connected to the polydiene backbone.

Results and Discussion

Synthesis of 1. Monomer **1** was synthesized from 1-adamantanecarboxylic acid (**2**) via the four-step reaction in 29% yield, as illustrated in Scheme 2. At first, **2** was converted into the acid chloride (**3**) by treating with thionyl chloride. Next, **3** was reacted with methylmagnesium iodide in the presence of copper(I) chloride to form 1-adamantyl methyl ketone (**4**). The ketone **4** was then treated with vinylmagnesium bromide in THF to give an alcohol (**5**). The dehydration of **5** under acidic conditions finally gave a target monomer **1**. The 1,3-diene monomer **1** was purified by the flash column chromatography and by the following fractional vacuum distillations over CaH_2. The purity of **1** was analyzed to be over 99% by the GLC and NMR measurements. Further distillation of **1** over *n*-BuLi was carried out on a vacuum line prior to the anionic polymerization.

It is reported that the anionic polymerizability of vinyl monomers can be predicted by the β-carbon chemical shifts of vinyl groups in the ^{13}C NMR spectra, which reflect the electron densities of the C=C bonds.[13] We herein predict the anionic polymerizability of **1** relative to that of isoprene from their ^{13}C NMR chemical shifts of butadienyl skeletons. The ^{13}C NMR signals of C_4 carbon ($-CH{=}CH_2$) and C_1 carbon ($-C(Ad){=}CH_2$) for **1** were observed at 114.8 and 107.1 ppm, respectively. These values were located at the upfield region compared with the chemical shifts of C_4 and C_1 carbons for isoprene at 116.8 and 113.6 ppm. Both upfield chemical shifts of **1** suggest the relatively high electron density of 1,3-diene framework of **1** compared with isoprene. In addition, the electron densities of C_1 and C_4 are highly biased probably due to the electronic and steric effects of the adamantyl substituent on C_2 carbon. This means that the anionic polymerization of **1** tends to proceed in a regioselective fashion on the 1,3-diene framework similar to the case of isoprene.[11] The nucleophilic attack of initiator and the propagating carbanion will take place toward the C_4 carbon of **1** to form the conjugated allyl anion (Scheme 3). From the resulting allyl anion, the nucleophilic propagation will preferentially occur from the C_1 carbanion to the C_4 carbon of **1**, not from the hindered C_3 carbanion. Therefore, the monomer addition mode of **1** should be highly regulated to a 4,1-mode. In fact, the major repeating unit of poly(**1**) was 1,4-microstructure in most cases regardless of the polymerization conditions, as discussed later.

Anionic Polymerization of 1. We first attempt to polymerize **1** with *s*-BuLi as an initiator in hydrocarbons such as *n*-heptane or cyclohexane at 40 °C, as shown in Table 1. On the addition of **1** to the initiator, the system always showed a pale yellow or orange color. The color remained unchanged during the course of the polymerization but disappeared instantaneously by quenching with a small amount of degassed methanol. As the polymerization proceeded, white precipitate was observed in the polymerization system using *n*-heptane as a solvent, while the polymerization system was homogeneous in cyclohexane. Complete consumption of **1** was always achieved within 3−5 h, and the yield of polymer was quantitative. Although the resulting polymer was first soluble in several solvents such as $CHCl_3$ and THF, the white precipitate was observed in the solutions with time. Interestingly, the polymer became insoluble in any organic solvents after the precipitation in methanol.[14] Only the low molecular

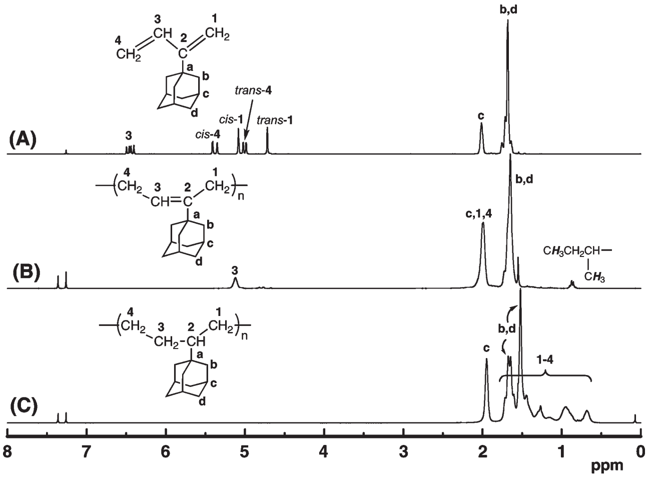


Figure 1. ^{1}H NMR spectra of **1** (A), poly(**1**) run 5, (B), and poly(E-*alt*-VAd) (C) measured in $CDCl_3$.

weight sample (run 1) was barely soluble in $CHCl_3$ and THF even after the precipitation in methanol. Then, we characterize the soluble sample by the ^{1}H and ^{13}C NMR measurements in the $CDCl_3$ solution. Figure 1 shows the ^{1}H NMR spectra of the starting monomer **1** (A) and the polymer obtained with *s*-BuLi in cyclohexane (B). The olefin proton signals of **1** between 4.7 and 6.5 ppm completely disappeared after the polymerization, and alternatively the new proton signals corresponding to the polydiene microstructures appeared between 4.6 and 5.2 ppm. The bridgehead methine protons on the adamantyl group and the methylene protons corresponding to the main chain were observed around 2.0 ppm, and methylene protons on the adamantyl group were present around 1.7 ppm. The CH_3 proton signal of the initiator residue, *sec*-butyl group, was observed at 0.8 ppm, as expected. The molecular weight of poly(**1**) was therefore estimated to be 2100 by using the signal intensities of initiator residue and the repeating units of poly(**1**) as shown in Table 1. The M_n estimated from ^{1}H NMR showed a good agreement with the calculated value based on the molar ratio between monomer and initiator (M_n(calcd) = 2000). This result supports the quantitative initiation efficiency of the polymerization system. In the ^{13}C NMR spectra (Figure 2), the signals at 107.1 (C1), 114.8 (C4), 136.5 (C3), and 157.3 ppm (C2) corresponding to the butadienyl framework of **1** completely disappeared after the polymerization. Alternatively, four signals for the C=C moiety (122.7 and 147.8 ppm) and methylene groups (27.9 and 30.4 ppm) in the main chain of polymer newly appeared. These strongly indicate that the anionic polymerization of **1** proceeded in hydrocarbons to afford the polymer possessing predominant 1,4-repeating unit, as discussed later.

For the higher molecular weight samples showing poor solubility, we carried out the quantitative hydrogenation of the C=C moiety of poly(**1**) with *p*-toluenesulfonhydrazide in order to increase the solubility,[15] as described later. After the complete hydrogenation, the polymer became readily soluble in the various solvents such as benzene, $CHCl_3$, and THF. Then, we could characterize the structure and the molecular weight of the hydrogenated polymers by using the NMR and SEC measurements in detail. The molecular weight data of the hydrogenated samples are shown in Table 1. Figure 3 shows a series of SEC traces of the hydrogenated polymers obtained in cyclohexane. The SEC traces shift toward higher molecular weight region with increasing the molar ratio between monomer and initiator, M/I. All the SEC traces are unimodal, but the high molecular weight samples show the significant tailing toward the low molecular weight region.[16] The polydispersity index, M_w/M_n, was within 1.1, indicating the narrow MWD of the low molecular weight polymer obtained in cyclohexane. On the other hand, the M_w/M_n values were around 1.3−1.4 for the high molecular weight samples, suggesting the relatively broad MWDs. The polymers obtained in *n*-heptane (runs 5−7) also showed similar tendency in the MWD depending on the M_n. On the other hand, the M_n value determined by the RALLS-SEC showed a good agreement with the calculated one in each polymer produced in hydrocarbons. The M_n of the lowest molecular weight sample (run 1) before hydrogenation was determined to be 2300 by the RALLS-SEC. This M_n value was close to the M_n(NMR) of 2100 and the calculated molecular weight of 2000. We thus conclude that the molecular weight control of polymer is attained in the anionic polymerization system of **1**. These results show that the anionic polymerization of **1** in hydrocarbons quantitatively proceeds to give the poly(**1**) with well-defined chain structures, whereas the MWD becomes slightly broader in the higher molecular weight samples.

Next, we attempted to polymerize **1** in a typical polar solvent of THF. The polymerization system showed a pale yellow color, when the THF solution of **1** was added to a solution of *s*-BuLi in *n*-heptane at −78 °C. After 24 h, the polymerization was quenched with a small amount of degassed methanol, and the yellow color disappeared instantaneously. The conversion of monomer was estimated by ^{1}H NMR, but only the monomer was observed in the reaction system (run 8). This is similar to the polymerization behavior of isoprene under the identical conditions. We have already confirmed that the completion of the anionic polymerization of isoprene with *s*-BuLi in THF requires a long reaction time for 72 h even at −30 °C. We then elevated the polymerization temperature to −30 °C to realize the polymerization of **1** in THF (run 9). The complete consumption of **1** was achieved at −30 °C after 72 h in the homogeneous system, and the polymer was quantitatively obtained. The SEC trace of the resulting polymer was unimodal and fairly narrow, and the M_w/M_n value was 1.07. The molecular weight measured by ^{1}H NMR (M_n = 2400) was identical with the M_n value of RALLS-SEC, and they were close to the calculated one (M_n = 2100).

We finally polymerized **1** with potassium naphthalenide, a typical difunctional initiator, in THF at −78 °C. The polymerization proceeded in the homogeneous system. The conversion was very low (28%) after 3 h (run 10), but all the monomer was consumed after 24 h (runs 11 and 12). The resulting poly(**1**)s possessed the narrow MWDs, although the observed M_ns were slightly higher than the calculated ones. In the case of anionic polymerization of isoprene with potassium naphthalenide in THF, the complete consumption of monomer is generally achieved at −78 °C within 3 h to give a well-defined polyisoprene possessing a major 3,4-repeating unit.[9] The polymerization of **1**, 1,3-butadiene derivative carrying a bulky adamantyl group, is clearly much slower than that of isoprene, a methyl-substituted counterpart. It is noteworthy that both the nonpolar and polar solvents are effective to realize the controlled homopolymerization of **1** to afford the well-defined polydienes having an adamantyl substituent.

Block Copolymerization of 1 with Styrene. We then carried out the sequential block copolymerization of **1** with styrene in order to prove the living nature of the polymerization system as shown in Table 2.[17] All the block copolymerizations proceeded homogeneously, and the copolymers were

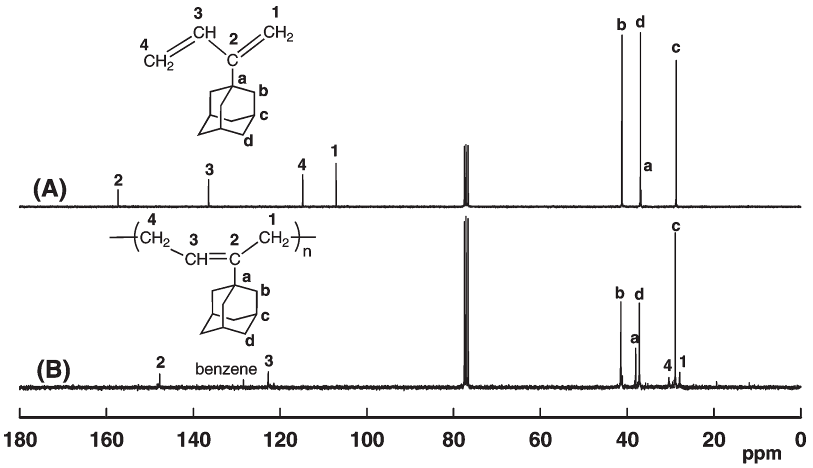


Figure 2. ^{13}C NMR spectra of **1** (A) and poly(**1**) run 5 (B) measured in $CDCl_3$.

Table 2. Block Copolymerization of 1 with Styrene[a]

				monomer (polymerization time, h)			block copolymer[c] (homopolymer[d])			
							M_n (kg/mol)			
run	solvent	temp[b] (°C)	initiator	1st	2nd	block sequence	calcd	RALLS	NMR[e]	M_w/M_n[f]
13	THF	−78	K-Naph	**1** (24)	styrene (1)	B−A−B	22 (11)	24 (11)	24	1.10 (1.07)
14	THF	−78	K-Naph	styrene (1)	**1** (24)	A−B−A	20 (9.9)	21 (11)	20	1.04 (1.04)
15	THF	−30	*s*-BuLi	styrene (1)	**1** (72)	B−A	15 (8.9)	14 (9.0)	14	1.04 (1.04)
16	cyclohexane	40	*s*-BuLi	**1** (3)	styrene (1)	A−B	16 (5.7)	17 (6.3)	21	1.09 (1.25)
17	cyclohexane	40	*s*-BuLi	styrene (1)	**1** (3)	B−A	10 (5.2)	11 (5.2)	10	1.05 (1.03)

[a] Polymer yields were quantitative in all cases. [b] Polymerization temperature for **1**. [c] Data before hydrogenation. [d] Homopolymers were obtained from first monomers. [e] M_n(NMR) was determined by using the molecular weight of the homopolymer and the composition of the block copolymer analyzed by ^{1}H NMR. [f] M_w/M_n was obtained by SEC calibration using polystyrene standards in THF solution. [g] Data after hydrogenation.

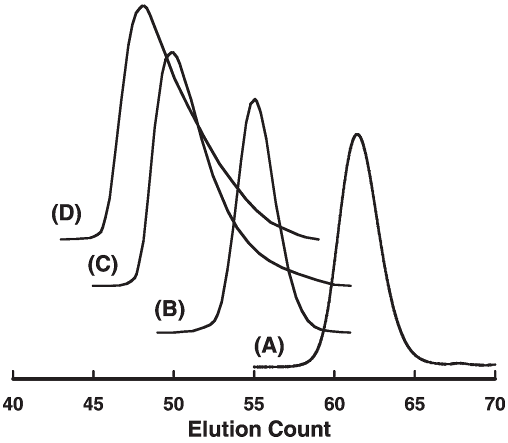


Figure 3. SEC traces of hydrogenated P(E-*alt*-VAd) obtained with *s*-BuLi in cyclohexane: peak (A) run 1, (poly(**1**) before hydrogenation), M_n(calcd) = 2000 g/mol, M_n(RALLS) = 2300 g/mol, M_w/M_n = 1.08; peak (B) run 2, M_n(calcd)=5100 g/mol, M_n(RALLS)=6000 g/mol, M_w/M_n = 1.09; peak (C) run 3, M_n(calcd) = 10 000 g/mol, M_n(RALLS) = 11 000 g/mol, M_w/M_n=1.31; peak (D) run 4, M_n(calcd)= 19 000 g/mol, M_n(RALLS) = 21 000 g/mol, M_w/M_n = 1.38.

obtained in quantitative yields. Since the resulting copolymers were soluble in various organic solvents such as THF and $CHCl_3$ at ambient temperature, the structure and composition were readily characterized by NMR measurement without the hydrogenation of poly(**1**) segment. The M_n values of block copolymers possessing poly(**1**) segments were estimated from either RALLS-SEC or ^{1}H NMR measurement.

At first, the polymerization of **1** was performed with potassium naphthalenide in THF at −78 °C for 24 h to achieve the quantitative conversion. After complete consumption of **1**, styrene was added to the difunctional poly (**1**) anion to further propagate the copolymerization. The color of polymerization system rapidly changed from yellow to deep red on the addition of styrene, indicating that the instantaneous crossover initiation occurred. The copolymer was obtained quantitatively after quenching with methanol after 1 h. Figure 4 shows the SEC traces of the hydrogenated poly(**1**) and the copolymer. The SEC trace of copolymer shifts toward the higher molecular weight region from the SEC trace of hydrogenated poly(**1**) with keeping the

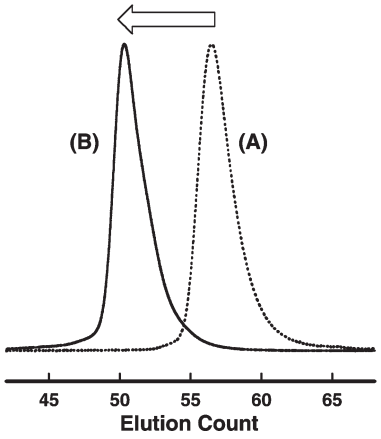


Figure 4. SEC traces of hydrogenated P(E-*alt*-VAd) run 13, (A, dotted line) and poly(styrene-*b*-**1**-*b*-styrene) (B, solid line): peak (A), M_n(calcd)= 11 000 g/mol, M_n(RALLS)= 11 000 g/mol, M_w/M_n= 1.07; peak (B), M_n(calcd)= 22 000 g/mol, M_n(RALLS)= 24 000 g/mol, M_w/M_n= 1.10.

Table 3. Microstructure of Polymers[a]

							microstructure (%)[d]			
				monomer			1,4-			
run	polymerization condition M^{+}/solvent	DP[b]	M_n[c] (kg/mol)	1st	2nd	block sequence	*cis*-	*trans*-	3,4-	1.2-
1	Li^{+}/cyclohexane[e]	11	2.3	**1**			89	7	2	2
5	Li^{+}/*n*-heptane[f]	13	3.1	**1**			86	7	4	3
9	Li^{+}/THF[g]	16	2.4	**1**			72	16	10	2
11	K^{+}/THF[h]	12	4.3	**1**			39	16	45	
13	K^{+}/THF[h]	29	11	**1**	styrene	B−A−B	57	22	21	
14	K^{+}/THF[h]	29	11	styrene	**1**	A−B−A	82	12	4	2
15	Li^{+}/THF[i]	48	9.0	styrene	**1**	B−A	29	11	60	
16	Li^{+}/cyclohexane[e]	34	6.3	**1**	styrene	A−B	81	14	5	
17	Li^{+}/cyclohexane[e]	28	5.2	styrene	**1**	B−A	77	19	3	1
Isp-1	Li^{+}/cyclohexane[e]	85	5.8	isoprene			95		5	~0
Isp-2	Li^{+}/THF[g]	266	18	isoprene			~0		80	20
Isp-3	K^{+}/THF[h]	368	25	isoprene			10		57	33

[a] Determined by ^{1}H NMR. [b] Degree of polymerization of poly(**1**) segment. [c] Molecular weight of poly(**1**) segment estimated by RALLS-SEC and ^{1}H NMR. [d] The ^{1}H NMR signals were assigned as follows: 5.13 ppm = *cis*-1,4-; 5.05 ppm = *trans*-1,4-; 4.82 ppm = 3,4-; 4.77 ppm = 3,4- + 1,2-; and 4.68 ppm = 1,2-. [e] Polymerized in cyclohexane at 40 °C with *s*-BuLi. [f] Polymerized in *n*-heptane at 40 °C with *s*-BuLi. [g] Polymerized in THF at −30 °C with *s*-BuLi. [h] Polymerized in THF at −78 °C with K-Naph. [i] Styrene was first polymerized in THF at −78 °C with *s*-BuLi, and then second monomer of **1** was polymerized at −30 °C.

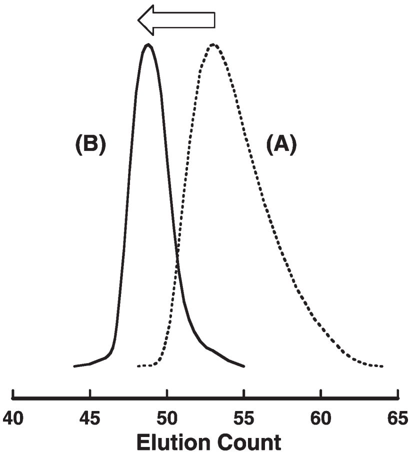


Figure 5. SEC traces of hydrogenated P(E-*alt*-VAd) run 16 (A, dotted line) and poly(**1**-*b*-styrene) (B, solid line): peak (A), M_n(calcd) = 5700 g/mol, M_n(RALLS) = 6300 g/mol, M_w/M_n = 1.25; peak (B), M_n(calcd) = 16 000 g/mol, M_n(RALLS) = 17 000 g/mol, M_w/M_n = 1.09.

unimodal and narrow MWD. The composition and M_n of triblock copolymer determined by the NMR measurement agreed with the calculated values, as expected. These results clearly indicate the formation of well-defined ABA triblock copolymer of **1** and styrene, polystyrene-*b*-poly(**1**)-*b*-polystyrene. In addition, the stability of the propagating carbanion of poly(**1**) is demonstrated in THF at −78 °C at least for 24 h.

We next attempted the sequential copolymerization of **1** and styrene in cyclohexane. In the first stage, polymerization of **1** was initiated with *s*-BuLi at 40 °C for 1 h. The polymerization of styrene was successively carried out for 3 h at 40 °C. The yield of block copolymer was quantitative, and the block copolymer possessed the predicted composition and molecular weight. As can be seen in Figure 5, the SEC trace of poly(**1**)-*b*-polystyrene is unimodal and narrow and apparently shifts from the SEC trace of hydrogenated homopoly(**1**). These results support the living character of the propagating poly(**1**) anion in cyclohexane under the applied reaction conditions.

We then employed **1** as a second monomer to synthesize various block copolymers in the reversed sequences (runs 14, 15, and 17). In the first stage, difunctional or monofunctional living polystyrene as macroinitiator was prepared either with potassium naphthalenide in THF at −78 °C or with *s*-BuLi in cyclohexane at 40 °C, respectively. After the addition of **1** to the living polystyrene, the polymerization of **1** smoothly proceeded either in THF or in cyclohexane to produce the block copolymer of styrene and **1**. In each case, the block copolymer with tailored molecular architectures such as predicted composition and M_n and narrow MWD was quantitatively obtained. The results obtained in this section demonstrate the comparable polymerizability of **1** and styrene, since the reversible sequential copolymerization of **1** and styrene is possible to produce the tailored block copolymers.

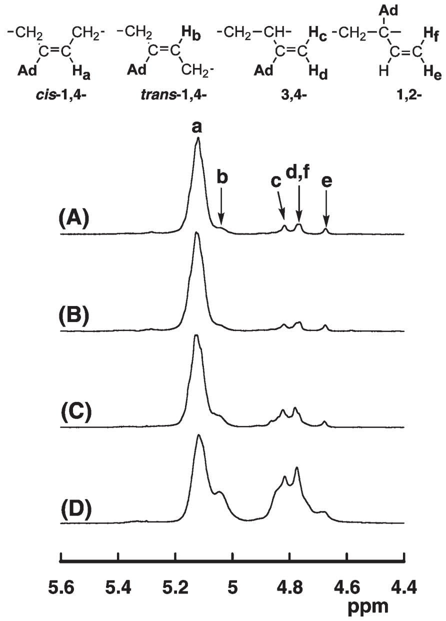


Figure 6. ^{1}H NMR spectra of olefinic protons of poly(**1**): (A) run 5, Li^{+}/*n*-heptane; (B) run 1, Li^{+}/cyclohexane; (C) run 9, Li^{+}/THF; (D) run 11, K^{+}/THF.

Microstructure of Polymers. It is well-known that the microstructures of the polydienes anionically produced are strongly influenced by the conditions such as solvent, counterion, and polymerization temperature.[11,18] For example, the polymerizations of isoprene with alkyllithium initiators in nonpolar hydrocarbons usually afford the polymers with

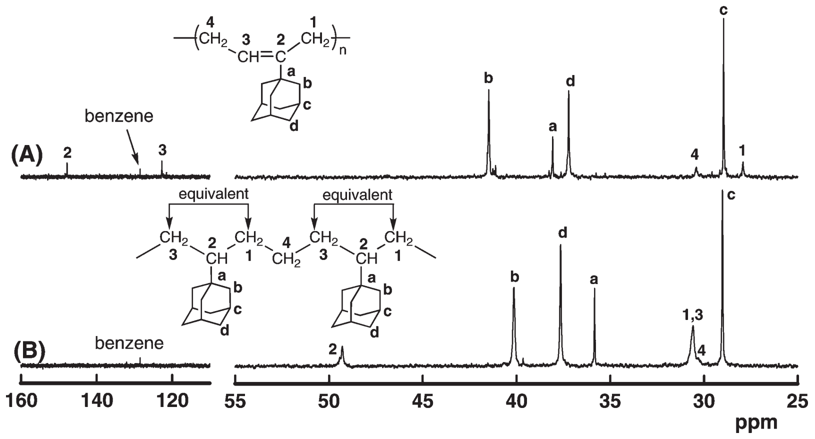
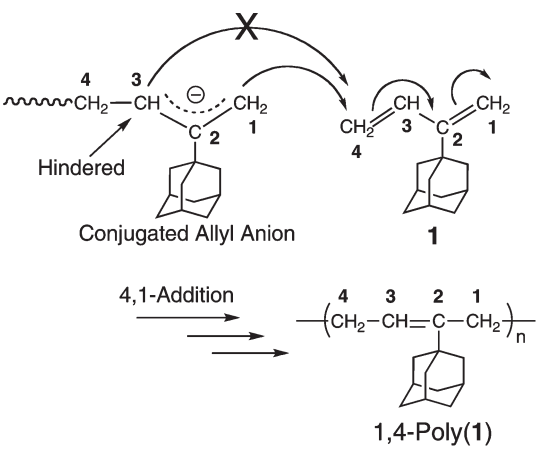


Figure 7. ^{13}C NMR spectra of poly(**1**) run 5 (A) and P(E-*alt*-VAd) (B) measured in CDCl$_3$.

Scheme 3. Possible Addition Mode of 1



high 1,4-microstructure contents, as shown in Table 3 (run Isp-1). On the other hand, the microstructures of polyisoprene dramatically changed to a mixture of 3,4-, 1,2-, and 1,4-addition modes, if the polymerization was carried out in polar solvents such as THF (runs Isp-2 and Isp-3). In addition, the substituents strongly affect the microstructures of a series of poly(2-alkyl-1,3-butadiene)s.[18] The 1,4-microstructure contents of the polymers obtained with *n*-BuLi in a polar solvent of diethyl ether increased with the bulkiness of the 2-substituted alkyl groups. The observed 1,4-contents for polymers of 2-ethyl-, 2-propyl-, 2-(*n*-butyl)-, and 2-isopropyl-1,3-butadienes were 58, 57, 56, and 81%, respectively, while that of polyisoprene, the 2-methyl counterpart, was only 19% under the identical polymerization conditions.

Microstructures of poly(**1**)s synthesized in this study are summarized in Table 3. The low molecular weight samples soluble in CDCl$_3$ were used for the discussion of microstructures measured by ^{1}H NMR. Figure 6 show a series of ^{1}H NMR spectra of olefinic region of poly(**1**)s. The five olefinic proton signals attributed to 1,4-, 1,2-, and 3,4-microstructures appear at 4.6−5.2 ppm similar to the ^{1}H NMR spectra of polyisoprene. We have assigned the observed five signals as *cis*-1,4- (5.13 ppm), *trans*-1,4- (5.05 ppm), 3,4- (4.82 ppm), 3,4- and 1,2- (4.77 ppm), and 1,2- (4.68 ppm) by comparing the assignments of polyisoprene[11] and various *cis*- and *trans*-alkenes, as shown in Figure 6. The integral ratios of these signals were determined by curve-fitting methods of five peaks.

As for poly(**1**)s obtained with Li$^+$/hydrocarbon systems, the major microstructure was 1,4-mode regardless of the solvent. The contents of 1,4-microstructures were 93% (in *n*-heptane) and 96% (in cyclohexane). In particular, the *cis*-1,4-content was predominant and over 85% in each case. The 1,4-rich polymers of 2-alkyl-1,3-butadienes possessing methyl-, ethyl-, propyl-, isopropyl-, and *n*-butyl groups have been similarly obtained with *n*-BuLi in *n*-heptane.[18] In the case of poly(**1**) produced with Li$^+$/THF system (run 9), the major was still 1,4-microstructure similar to the Li$^+$/hydrocarbon system, while the content slightly decreased to 88%. On the other hand, *trans*-1,4- and 3,4- contents increased to 16 and 10%, respectively. These observations largely differ from the polymerization of isoprene, which affords 3,4- and 1,2-microstructures in 80 and 20%, respectively (run Isp-2). In this case, the content of 1,4-microstructure was negligible. The bulkiness of 2-substituted adamantyl group of **1** might play a role to induce the high 1,4-content similar to the previous reports,[18,19] even the polymerization of **1** was carried out in a polar solvent of THF. When we changed the countercation from lithium to potassium in THF (run 11), the content of 1,4-microstructure in poly(**1**) decreased to 55%, and the vinyl addition modes including 3,4- and 1,2-repeating units markedly increased to 45%. However, the 1,4-content is still higher than the polyisoprene (run Isp-3) obtained under the identical polymerization conditions, indicating the steric effect of adamantyl groups.

The microstructures of poly(**1**) segment in the block copolymers with styrene were similarly investigated by ^{1}H NMR measurement, as shown in Table 3. The poly(**1**) segments in the block copolymers obtained with organolithium in hydrocarbons also possessed high 1,4-contents (runs 16 and 17) regardless of the sequence of copolymers, similar to the homopoly(**1**)s. However, the 1,4-content in polystyrene-*b*-poly(**1**) prepared with *s*-BuLi in THF (run 15) was only 40% and considerably lower than that of the corresponding homopolymer (run 9, 1,4- = 88%). The polystyrene segment prepared in the first stage might play a role to change the microstructures of poly(**1**) segment in the sequential copolymerization. On the other hand, the polymerization system of organopotassium initiator in THF gave the poly(**1**) segments rich in 1,4-modes between 79 and 94% (runs 13 and 14), while the homopolymerization of **1** provided the 1,4-content in 55% under the conditions.

We finally mention the content of 1,2-microstructure. Only a few percent of the ^{1}H NMR signal derived from 1,2-microstructure was observed in each polymer sample. This suggests that the anionic species preferentially attack the C$_4$ carbons showing lower electron density (Scheme 3), and the monomer insertion predominantly occurs via a 4,1-mode similarly to the anionic polymerization of isoprene.

Synthesis of P(E-*alt*-VAd) via Hydrogenation of Poly(1). As mentioned before, we have succeeded in the complete hydrogenation of the poly(**1**)s to realize the practical solubility suitable for the various characterizations. Herein, the procedure of hydrogenation and the detailed characterization of the hydrogenated polymer are described to further confirm the microstructure of the parent poly(**1**). We carried out the hydrogenation of unsaturated functionality with *p*-toluenesulfonhydrazide in *o*-xylene under reflux (Scheme 1).[15] The reaction system was initially heterogeneous even at 140 °C and changed to a yellow homogeneous solution during the reduction. The polymer was obtained by the reprecipitations and the subsequent freeze-drying from benzene solution. The resulting hydrogenated polymers were white solids and were soluble at room temperature in a variety of common organic solvents such as THF, $CHCl_3$, and benzene. The completion of hydrogenation was confirmed by ^1H and ^{13}C NMR and IR measurements as well as RALLS-SEC.

We here employed the low molecular weight poly(**1**) sample synthesized with *s*-BuLi in *n*-heptane for the NMR measurement because of the acceptable solubility and the predominant 1,4-microstructure discussed above. Figures 1B and 1C show the ^1H NMR spectra of polymers before and after the hydrogenation. After the reaction, the signals due to the olefinic protons between 4.6 and 5.2 ppm completely disappear, and signals of methylene and methine protons in the main chain are newly observed between 0.6 and 1.7 ppm. In addition, the original methylene proton signals on the adamantyl ring at 1.7 ppm clearly split into the signals at 1.5 and 1.7 ppm after hydrogenation. Figure 7A shows the ^{13}C NMR spectrum of poly(**1**) before the hydrogenation. The observed eight major signals can be assigned to four carbons for adamantyl pendant group and other four carbons for the main chain of 1,4-poly(**1**) at 147.8, 122.7, 30.4, and 27.9 ppm. It is noteworthy that the *cis*-1,4-polyisoprene (Table 3, run Isp-1) shows similar four main chain signals at 135.3, 125.2, 32.2, and 26.5 ppm. We therefore considered that the signal of adamantyl-substituted carbon at 147.8 ppm markedly shifted to the downfield comparing with the corresponding methyl-substituted carbon for 1,4-polyisoprene at 135.3 ppm. In Figure 7B, two olefinic signals in the main chain at 147.8 and 122.7 ppm completely disappear after the hydrogenation, and seven signals are observed in the aliphatic region. These seven signals can be assigned to three carbons due to the saturated main chain at 30.3 (methylene), 30.6 (methylene), and 49.3 ppm (methine) and other four carbons derived from the adamantyl substituent. Two carbons, C_1 and C_3, in the main chain become equivalent after the hydrogenation, since the repeating unit of poly(**1**) predominantly consists of 4,1-addition mode. Thus, the spectroscopic observations confirm that the quantitative hydrogenation of 1,4-poly(**1**) gives a novel alternating copolymer of ethylene and 1-vinyladamantane, P(E-*alt*-VAd), as shown in Scheme 1. The simple ^{13}C NMR spectrum also indicates that the propagation of **1** in hydrocarbons exclusively proceeds in the 4,1-addition modes via the regioselective attack of C_4-carbon of **1**, as described before (Scheme 3).

Figure 8 shows the SEC traces of polymers measured in THF before and after the hydrogenation. Although the theoretical increment of molecular weight by the quantitative hydrogenation is only 1 wt %, the SEC trace of the hydrogenated polymer, P(E-*alt*-VAd), significantly shifts toward the higher molecular weight region with maintaining the unimodal shape of the original poly(**1**). This reflects the remarkable change in hydrodynamic volume of the hydrogenated polymer regardless of the small increase of molecular weight. In fact, the observed molecular weights of polymers measured by RALLS-SEC before and after the hydrogenation were in good agreements with the calculated ones. These results clearly demonstrate that the quantitative conversion of 1,4-poly(**1**) into P(E-*alt*-VAd) occurs without any side reactions such as main chain degradation and cross-linking. We substantiate that the novel alternating hydrocarbon copolymer of P(E-*alt*-VAd) with well-defined chain structures is synthesized via the living anionic polymerization of **1** in the 4,1-addition mode, followed by the quantitative hydrogenation.

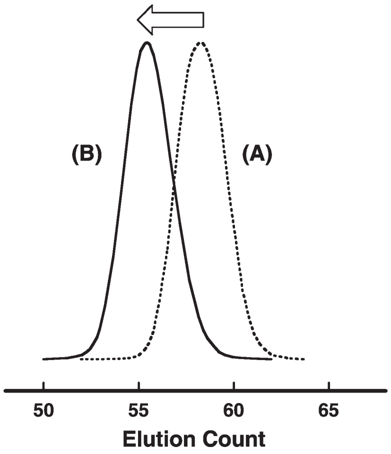


Figure 8. SEC traces of poly(**1**) run 5 (A, dotted line) and P(E-*alt*-VAd) (B, solid line): peak (A), M_n(SEC) = 2400 g/mol, M_w/M_n = 1.08; peak (B), M_n(RALLS) = 3100 g/mol, M_w/M_n = 1.08.

Solubilities and Thermal Properties. The solubilities of polymers obtained in this study are shown in Table 4, along with those of polyisoprene and its hydrogenated analogue poly(ethylene-*alt*-propylene) (P(E-*alt*-E)). The solubility of poly(**1**) was significantly lower than that of polyisoprene and was affected by the employed polymerization systems such as initiator and solvent. The 1,4-poly(**1**) obtained with *s*-BuLi in cyclohexane showed a solubility depending on the molecular weight. The low molecular weight sample (run 1, DP = 12) was soluble in the various organic solvents, while the solubility decreased with the degree of polymerization. The highest molecular weight sample (run 4, DP = 112) was partially soluble in carbon tetrachloride but insoluble in other organic solvents. In fact, this sample was insoluble even in toluene, xylenes, and 1,2-dichlorobenzene at the elevated temperature. On the other hand, poly(**1**) obtained with K-Naph in THF (run 12, DP = 85) was soluble in cyclohexane, benzene, carbon tetrachloride, and $CHCl_3$ and partially soluble in THF. We now consider that this significant difference in solubility is derived from the microstructure of the polymer depending on the polymerization conditions (Table 3). For example, the content of 1,4-microstructure was 96% (Li^+/cyclohexane) and 55% (K^+/THF). The higher 1,4-content of the repeating unit induces the lower solubility of poly(**1**). The stiff and planar C=C−Ad moieties in the 1,4-microstructure might interfere with the movement of polymer main chain to result in the lower solubility.

By contrast, the hydrogenated 1,4-poly(**1**), P(E-*alt*-VAd), showed a good solubility in the various solvents such as cyclohexane, benzene, carbon tetrachloride, $CHCl_3$, and THF. The low molecular weight P(E-*alt*-VAd) and the sample obtained with K^+/THF system were soluble even in *n*-hexane, also indicating the effects of molecular weight and microstructure. After the hydrogenation, the flexible saturated main chain of P(E-*alt*-VAd) might gain the

Table 4. Solubility of Polymers (S: Soluble; P: Partially Soluble; I: Insoluble)

	polydiene					hydrogenated polymer		
	poly(**1**)				polyisoprene[a]	hydrogenated poly(**1**)		
run	1[a]	2[a]	4[a]	12[b]		4hyd[a]	12hyd[b]	P(E-*alt*-P)[a]
counterion[c]	Li^+	Li^+	Li^+	K^+	Li^+	Li^+	K^+	Li^+
solvent[d]	cyclohexane	cyclohexane	cyclohexane	THF	cyclohexane	cyclohexane	THF	cyclohexane
M_n(RALLS) (kg/mol)	2.3	6.0	21	16	6.0	21	16	6.0
DP[e]	12	32	112	85	88	112	85	88
n-hexane	S	I	I	I	S	I	S	S
cyclohexane	S	I	I	S	S	S	S	S
benzene	S	P	I	S	S	S	S	S
CCl_4	S	P	P	S	S	S	S	S
$CHCl_3$	S	P	I	S	S	S	S	S
ethyl acetate	I	I	I	I	I	I	I	I
1,4-dioxane	S	I	I	I	I	I	I	I
THF	S	P	I	P	S	S	S	S
DMF	I	I	I	I	I	I	I	I
methanol	I	I	I	I	I	I	I	I
water	I	I	I	I	I	I	I	I

[a] Polymerized in cyclohexane at 40 °C with *s*-BuLi. [b] Polymerized in THF at −78 °C with K-Naph. [c] Counterion of initiator. [d] Solvent of polymerization. [e] Degree of polymerization.

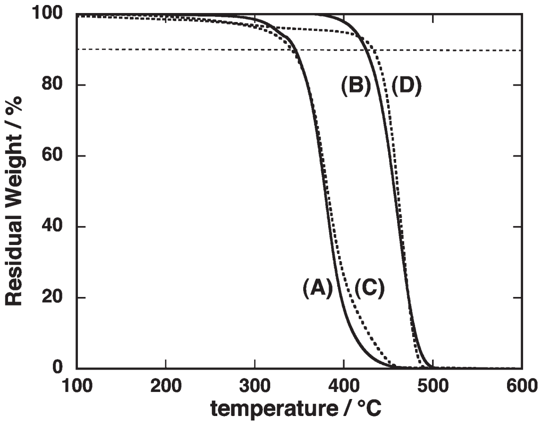


Figure 9. TGA thermograms of polymers under nitrogen flow with a heating rate of 10 °C min^{-1}: (A) poly(**1**), T_{10} = 345 °C; (B) P(E-*alt*-VAd), T_{10} = 425 °C; (C) 1,4-polyisoprene, T_{10} = 341 °C; (D) P(E-*alt*-P), T_{10} = 433 °C.

higher affinity to the organic solvents and the rapid chain motion.

Thermal stability of the resulting polymers was investigated by thermogravimetric analysis (TGA) under nitrogen. Figure 9 shows a series of TGA thermograms of 1,4-poly(**1**), 1,4-polyisoprene, and their hydrogenated polymers. Poly(**1**) and polyisoprene show similar decomposition behaviors, and the degradations start around 280 °C on heating. The 10% weight loss temperatures (T_{10}) of poly(**1**) and polyisoprene were 345 and 341 °C, and both unsaturated polymers completely decomposed around 460 °C. On the other hand, the thermal stabilities of the corresponding hydrogenated polymers, P(E-*alt*-VAd) and P(E-*alt*-P), were significantly enhanced due to the absence of C=C double bonds. In fact, the thermal decomposition of P(E-*alt*-VAd) started from 380 °C, and the complete weight loss was observed at 490 °C. T_{10}s of P(E-*alt*-VAd) and P(E-*alt*-P) were observed at 425 and 433 °C, respectively. These results indicate that the thermal stability of the polymer is mainly dominated by the main chain structures not by the side chain substituents.

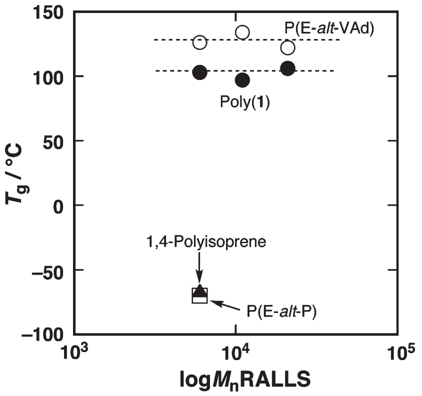


Figure 10. Relationship between M_n and T_g of poly(**1**) (●), P(E-*alt*-VAd) (○), 1,4-polyisoprene (▲), and P(E-*alt*-P) (□).

The glass transition behavior of poly(**1**) and P(E-*alt*-VAd) was analyzed by differential scanning calorimetry (DSC). All the poly(**1**) samples possessed the 1,4-repeating units, since they were anionically synthesized in cyclohexane. Figure 10 shows the dependence of T_g values on the molecular weight, along with those of polyisoprene and its hydrogenated polymer. In each case, only one glass transition behavior was observed in the DSC profile, and no melting transition was detected before the thermal degradation. The T_gs of poly(**1**)s were observed around 100 °C, and the hydrogenated P(E-*alt*-VAd)s presented slightly higher T_gs around 125 °C. On the other hand, 1,4-polyisoprene showed an extremely low T_g at −70 °C, and its hydrogenated polymer, P(E-*alt*-P), also exhibited a low T_g at −66 °C. The substitution of methyl group with bulky and stiff adamantyl group drastically raises the T_g values by 170−190 °C.

Conclusions

We have succeeded in the living anionic polymerization of a novel adamantyl-substituted 1,3-butadiene, **1**. Polymerizations of **1** in cyclohexane and THF quantitatively proceed in the homogeneous systems to give the homopolymers with regulated chain lengths. A series of well-defined AB, BA, ABA, and BAB block copolymers are quantitatively synthesized by the reversible sequential copolymerization of **1** with styrene. Interestingly, the microstructure of poly(**1**) is controlled to be 1,4-rich in most cases, even if the polymerization is performed in polar solvent such as THF. The bulky adamantyl group on 1,3-diene framework plays a very important role to induce the regioselective propagation and the 1,4-repeating unit. The complete hydrogenation with *p*-toluenesulfonhydrazide converts 1,4-poly(**1**) into the novel aliphatic alternating copolymer, P(E-*alt*-VAd). The resulting poly(**1**) and P(E-*alt*-VAd) show high T_g values at 100 and 125 °C, indicating the drastic substituent effect of adamantyl skeleton. Thus, the living anionic polymerization of **1**, adamantyl-substituted 1,3-butadiene, and the subsequent hydrogenation opens the new synthetic pathways for the high-performance polymeric materials as well as the anionic polymerizations of 4-(1-adamantyl)styrene[9,10] and 1-adamantyl and 3-(1,1′-biadamantyl) methacrylates.[8]

Experimental Section

Materials. All reagents were purchased from Tokyo Kasei, unless otherwise stated. Diethyl ether was dried over sodium wire. Styrene was washed with 5% NaOH aqueous solution and with water and dried over anhydrous $MgSO_4$. It was then distilled over CaH_2 under vacuum. *n*-Heptane and cyclohexane were washed with concentrated H_2SO_4, dried over $MgSO_4$, and then dried over P_2O_5 for 1 day under reflux. It was then distilled in the presence of *n*-BuLi under nitrogen. THF used as a polymerization solvent was refluxed over sodium wire for 3 h, distilled over $LiAlH_4$, and further distilled from sodium naphthalenide solution on a vacuum line. Other commercially available reagents were used without further purification.

Initiators. Commercially available *s*-BuLi (1.0 M in cyclohexane, Kanto Chemical Co., Inc.) was used without purification and diluted with dry *n*-heptane or dry cyclohexane. Potassium naphthalenide was prepared by the reactions of a small excess of naphthalene with potassium in THF. These initiators were sealed off under high-vacuum conditions in ampules equipped with break-seals and stored at −30 °C. The concentration of initiator was determined by colorimetric titration using standardized 1-octanol in THF in a sealed reactor under vacuum, as previous reported.[20]

1-Adamantyl Methyl Ketone (4). Methylmagnesium iodide was prepared by the reaction of methyl iodide (16.7 g, 118 mmol) and magnesium (4.23 g, 174 mmol) in diethyl ether (130 mL). A mixture of thionyl chloride (40 mL) and 1-adamantanecarboxylic acid (**2**) (Aldrich, 18.4 g, 102 mmol) was stirred at 80 °C for 2 h. Then, excess amount of thionyl chloride was removed in vacuo. Dry toluene (40 mL) was added to the residue, and a trace of thionyl chloride was azeotropically removed to give a white solid of 1-adamantanecarbonyl chloride (**3**) at 40 °C under vacuum conditions. After complete removal of thionyl chloride and toluene, diethyl ether (100 mL) and CuCl (0.57 g, 5.7 mmol) were added to the solid under nitrogen. To the mixture, methylmagnesium iodide (118 mmol) in diethyl ether (130 mL) was added dropwise at 0 °C under nitrogen. The reaction mixture was stirred at room temperature for 30 min and then carefully quenched with 2 N HCl. The organic layer was separated, and the aqueous layer was extracted with diethyl ether three times. The combined organic layer was dried over anhydrous $MgSO_4$. After concentration of the solution, the resulting solid was purified by flash column chromatography (silica gel, hexane/dichloromethane = 9/1 v/v) to give white solid of **4** (15.6 g, 87.6 mmol, 86%, mp = 53−54 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.6−1.9 (m, 12H, C(b)H_2, C(d)H_2), 2.0−2.1 (m, 6H, C(c)H, $-CH_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.4 (CH_3), 28.0 (Cc), 36.6 (Cd), 38.3 (Cb), 46.6 (Ca), 214.3 (C═O).

2-(1-Adamantyl)-3-buten-2-ol (5). A solution of vinyl bromide in THF (Aldrich, 1 M, 151 mL, 151 mmol) was added dropwise to magnesium (5.50 g, 260 mmol) activated with 1,2-dibromoethane in THF (30 mL) at 0 °C under nitrogen. The reaction mixture was stirred at 0 °C for 1 h and at room temperature for 1 h. A THF solution (100 mL) of **4** (24.3 g, 137 mmol) was added dropwise at 0 °C to the reaction system, and then the reaction mixture was stirred overnight at room temperature. The reaction was quenched with 2 N HCl under cooling at 0 °C. The reaction system was extracted with diethyl ether three times, and the combined organic layer was dried over anhydrous $MgSO_4$. After concentration of the solution, a colorless liquid of **5** (27.6 g) was obtained. The crude product was used for the next reaction step without isolation.

2-(1-Adamantyl)-1,3-butadiene (1). A catalytic amount of *p*-toluenesulfonic acid (20 mg) was added to the solution of **5** (27.6 g) in benzene (150 mL), and the mixture was refluxed for 2 h with azeotropic separation of water by means of a Dean−Stark water trap. After cooling, the reaction mixture was washed with 5% NaOH aqueous solution twice. The organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the crude product was purified by flash column chromatography (silica gel, hexane). The product was further purified by the vacuum fractional distillation over CaH_2 to afford **1** (8.88 g, 47.2 mmol, 34% yield based on **4**, bp = 53−56 °C/0.25 mmHg) as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.63−1.79 (m, 12H, C(b)H_2, C(d)H_2), 2.01 (s, 3H, C(c)H), 4.72 (s, 1H, C(1)H_2= *trans*), 4.98−4.99 (d, 1H, C(4) H_2= *trans*, J = 12.9 Hz), 5.08 (s, 1H, C(1)H_2= *cis*), 5.35−5.41 (d, 1H, C(4)H_2= *cis*, J = 19.2 Hz), 6.40−6.49 (dd, 1H, =CH, J = 12.9 and 19.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.7 (Cc), 36.8 (Ca), 37.0 (Cd), 41.2 (Cb), 107.1 (C1), 114.8 (C4), 136.5 (C3), 157.3 (C2). IR (neat): 3085, 2900, 2848, 2680, 1604, 1449, 1421, 1243, 1225, 1102, 1076, 986, 910, 895, 818 cm^{-1}.

Purification of Monomers. After careful fractional distillations, monomers were degassed and sealed off in a glass apparatus equipped with a break-seal. For the purification of **1**, the sealed monomer was mixed with 1 mol % of *n*-BuLi (cyclohexane solution) and then distilled on a vacuum line into an ampule fitted with a break-seal. Dibutylmagnesium (2 mol %) in cyclohexane was used for the purification of styrene. The distilled monomer was finally diluted with dry solvents. The resulting monomer solutions (0.4−0.5 M) were stored at −30 °C until ready to use for the anionic polymerization.

Anionic Polymerization. Anionic polymerizations were carried in an all-glass apparatus equipped with break-seals with vigorous shaking under high-vacuum conditions (10^{-6} mmHg).[20] Polymerization was terminated with degassed methanol at the applied temperature, and the reaction mixture was poured into methanol to precipitate a polymer. Polymers collected by filtration were purified by reprecipitations/repeating washes in THF/methanol system and by freeze-drying from their benzene solutions.

Poly(1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.3−2.3 (19H, CH_2, C(b)H_2, C(c)H, C(d)H_2), 4.7−4.9 (2H, side chain, $-CH{=}CH_2$, $-C(Ad){=}CH_2$). 5.0−5.2 (1H, main chain, $-CH{=}C(Ad)-$). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 27.9 (C1), 28.9 (Cc), 30.4 (C4), 37.2 (Cd), 37.6 (Ca), 41.4 (Cb), 121.5 (C3), 147.8 (C2). IR (KBr): 2981, 2898, 2846, 1540, 1521, 1456, 1340, 1315, 1097, 1082, 858, 811 cm^{-1}.

Hydrogenation of Polymers. Poly(**1**) (100 mg, 0.53 mmol of olefin unit), *p*-toluenesulfonhydrazide (Aldrich, 1.00 g, 4.9 mmol), and a small amount of 3,5-di-*tert*-butyl-4-hydroxytoluene (ca. 5 mg) were added to *o*-xylene (5 mL). The mixture was refluxed for 8 h and then cooled to room temperature. The reaction mixture was then poured into methanol to precipitate a polymer. The precipitated polymer was isolated by filtration and further purified by repeating reprecipitation using the benzene/methanol system. After freeze-drying of the polymer from the benzene solution, P(E-*alt*-VAd) (72 mg, 0.38 mmol based on monomer unit, 72% yield) was obtained as a white powder. The hydrogenated polymer thus obtained was characterized by ^{1}H and ^{13}C NMR. The following is the complete list.

P(E-*alt*-VAd). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.6−1.8 (19H, CH_2 and CH (main chain), C(b)H_2, C(d)H_2), 1.9 (3H, C(c) H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.0 (Cc), 30.5 (C4), 30.6 (C1, C3), 35.8 (Ca), 37.6 (Cd), 40,1 (Cb), 49.3 (C2). IR (KBr): 2982, 2899, 2845, 1541, 1508, 1456, 1360, 1341, 1100, 1082, 973 cm^{-1}.

Polymer Characterization. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX300 spectrometer (300 MHz for ^{1}H and 75 MHz for ^{13}C) in $CDCl_3$. 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. IR spectra were recorded on a JASCO FT/IR-4100 instrument using either an attenuated total reflectance (ATR) attachment or the KBr disk method. SEC chromatograms for determination of molecular weight distribution were obtained in THF at 40 °C at a flow rate of 1.0 mL min^{-1} with a TOSOH HLC8020 instrument equipped with three polystyrene gel columns (TOSOH G5000H_{XL}, G4000H_{XL}, and G3000H_{XL}, measurable molecular weight range: $2 \times 10^3 - 4 \times 10^6$) with either ultraviolet (254 nm) absorption or refractive index detection. The M_n of polymers was 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 × 2 and TSKgel G2000H$_{HR}$) with triple detectors (RI, LS, and viscosity). THF was used as an eluent at 30 °C at a flow rate of 1.0 mL 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}. The T_g of the polymer was measured by DSC using a Seiko instrument DSC6220 apparatus under nitrogen flow. The polymer sample was first heated to 270 °C, cooled to −150 °C, and then scanned at a rate of 10 °C min^{-1}.

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