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Articles

Living Anionic Polymerizations of 4-(1-Adamantyl)styrene and 3-(4-Vinylphenyl)-1,1′-biadamantane

Shingo Kobayashi, Takahiro Matsuzawa, Shin-ichi Matsuoka, Hiroyuki Tajima, and Takashi Ishizone*

Department of Organic and Polymeric Materials, Tokyo Institute of Technology, 2-12-1-H-119, Ohokayama, Meguro-ku, Tokyo 152-8552 Japan

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ABSTRACT: Anionic polymerizations of new styrene derivatives, 4-(1-adamantyl)styrene (**1**) and 3-(4-vinylphenyl)-1,1′-biadamantane (**2**), were carried out with *sec*-butyllithium, cumylpotassium, and lithium- or potassium naphthalenide in THF at −78 °C for 3−4 h. The polymerizations of **1** and **2** 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 ($M_w/M_n = 1.03-1.13$). The stability of propagating chain ends of poly(**1**) and poly(**2**) was confirmed by the quantitative initiation efficiency in the sequential copolymerization of **1** and **2** with styrene or isoprene. Novel well-defined block copolymers, poly(**1**)-*b*-polystyrene, poly(**1**)-*b*-polyisoprene, poly(**1**)-*b*-polyisoprene-*b*-poly(**1**), poly(**2**)-*b*-polystyrene, and poly(**2**)-*b*-polyisoprene-*b*-poly(**2**), were anionically synthesized. The resulting poly(**1**) and poly(**2**) started to decompose over 340 °C and showed remarkably high glass transition temperatures (T_g) at 234 and 232 °C, respectively. The T_g values of anionically synthesized random copolymers of **1** and styrene could be changed between 100 and 230 °C by the feed molar ratio of comonomers. The incorporation of bulky and stiff adamantyl or 1,1′-biadamantyl moiety unequivocally induced the high thermal stability of novel 4-substituted polystyrenes, poly(**1**) and poly(**2**).

Introduction

Polystyrene-*b*-polybutadiene-*b*-polystyrene (SBS), polystyrene-*b*-polyisoprene-*b*-polystyrene (SIS), and the corresponding hydrogenated triblock copolymers are well-known and widely used as thermoplastic elastomers (TPE) exhibiting exellent mechanical strength properties.[1] These TPEs are usually synthesized via the anionic polymerization and consist of polystyrene hard segment and polydiene soft segment. The outer hard segements in TPE form spheric microdomains separated in the continuous soft polydiene phase and act as a cross-linker of physical network under the service conditions.

However, the current application of SBS and SIS is frequently limited by the glass transition temperature (T_g) of the hard segment, polystyrene blocks (100 °C). To solve this problem, considerable efforts have been paid to increase the T_g of glassy polystyrene domains in the SBS and SIS. Poly(4-*tert*-butylstyrene)[2] and poly(α-methylstyrene)[3] displaying higher T_g values (130 and 165 °C, respectively) are candidates for substitutions of polystyrene hard segments. However, the T_g value of the former one is not very high, and the low ceiling temperature of the latter polymerization system hinders the practical synthesis of triblock copolymer.

The T_g values of *p*-alkyl-substituted polystyrenes can be readily controlled either lower or higher by changing the substituent on the para position.[4,5] Linear alkyl substituents drastically decrease the T_g values of polymers with increasing side chain length, while the bulky substituents such as *tert*-butyl[2] or phenyl (161 °C)[6] groups tend to bring higher T_g values. It has been pointed out that both positioning the center of mass of substituents close to the polymer backbone and increasing the bulkiness of the substituent are very effective to increase the T_g values.[7]

In this study, we have newly designed and anionically polymerized two styrene derivatives, 4-(1-adamantyl)styrene (**1**)[8] and 3-(4-vinylphenyl)-1,1′-biadamantane (**2**), to prove the substituent effects of rigid and bulky adamantyl and 1,1-biadamantyl groups on thermal properties of the resulting polystyrenes. It has been reported that incorporation of adamantane skeleton in the backbone or as a pendant group into the condensation polymers[9] and vinyl polymers[10] show drastic changes in the chemical and physical properties. In particular, the introduced bulky adamantane ring usually gives the high T_gs and excellent thermal stabilities to the parent polymers. To our best knowledge, direct substitution effect of adamantyl groups on polystyrene backbone has not been investigated yet.[8,11]

We have recently succeeded in the living anionic polymerizations of alkyl methacrylates, 1-adamantyl methacrylates (**3**), and 3-methacryloyloxy-1,1′-biadamantane (**4**), to afford the well-defined homopolymers and block copolymers.[12] The resulting poly(**4**) exhibits a markedly high T_g value at 236 °C on the DSC thermograms and an enhanced thermal stability until 370 °C during the TGA analyses. On the other hand, no apparent glass transition behavior was observed for poly(**3**) prior to the thermal degradation around 370 °C. These certainly indicate the enormous substituent effects of adamantyl and 1,1′-biadamantyl moieties on the thermal properties. Since these bulky and rigid moieties are directly connected to the polystyrene backbone in

* Corresponding author. E-mail: tishizon@polymer.titech.ac.jp.

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Scheme 1

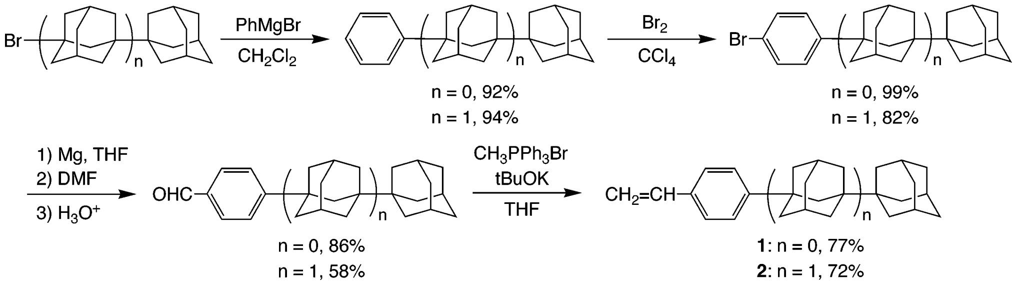


Table 1. Anionic Polymerization of 1 and 2 in THF at −78 °C[a]

run	monomer type, mmol	initiator type, mmol	time, h	$M_n \times 10^{-3}$ calcd[b]	$M_n \times 10^{-3}$ RALLS[c]	$M_n \times 10^{-3}$ SEC[d]	M_w/M_n[d]	T_g, °C
1	**1**, 3.29	*s*-BuLi, 0.0696	5 min	11	16	8.9	1.04	237
2	**1**, 2.46	*s*-BuLi, 0.124	3	4.7	4.6	3.2	1.04	221
3	**1**, 3.15	*s*-BuLi, 0.0613	3	12	13	8.4	1.06	231
4	**1**, 3.76	*s*-BuLi, 0.0604	3	15	17	8.8	1.06	238
5	**1**, 4.97	*s*-BuLi, 0.0458	1	26	26	15	1.03	234
6	**1**, 5.59	*s*-BuLi, 0.0245	8	54	57	37	1.03	233
7	**1**, 2.57	Li−Naph[e], 0.0980	3	12	18	10	1.05	247
8	**1**, 3.42	cumyl-K[f], 0.0972	3	8.4	11	6.6	1.05	228
9	**1**, 2.91	K−Naph[g], 0.139	3	10	14	7.6	1.10	233
10	**1**, 3.09	K−Naph, 0.131/α-MeSt[h], 0.246	3	12	14	7.9	1.13	233
11	**2**, 1.33	*s*-BuLi, 0.134	16	3.7	4.1	2.5	1.04	204
12	**2**, 1.00	*s*-BuLi, 0.0649	4	5.7	6.2	3.1	1.03	213
13	**2**, 1.78	*s*-BuLi, 0.0655	4	10	13	5.5	1.03	226
14[a, i]	**2**, 2.17	*s*-BuLi, 0.0446	16	18	44	14	1.07	232
15[i]	**2**, 1.16	K−Naph, 0.115	3	7.5	19	7.3	1.07	231
16[i]	**2**, 1.48	K−Naph, 0.0917	4	12	21	8.1	1.05	236
17	**2**, 1.17	K−Naph, 0.127/α-MeSt, 0.556	3	7.9	12	4.7	1.12	206

[a] Polymer yields were quantitative in all cases except for run 14 (conversion = 71%, yield = 70%). [b] M_n(calcd) = (MW of monomer) × [monomer]/[initiator] + MW of initiator residue. [c] M_n(RALLS) was obtained by RALLS−SEC using THF as an eluent. [d] M_n(SEC) and M_w/M_n were obtained by SEC caliblation using polystyrene standards in THF solution. [e] Lithium naphthalenide. [f] Cumylpotassium. [g] Potassium naphthalenide. [h] α-Methylstyrene. [i] The polymeric product was precipitated during the course of polymerizaion.

the cases of poly(**1**) and poly(**2**), more striking substituent effects on thermal and mechanical properties are expected.

Results and Discussion

Synthesis of 1 and 2. Monomer **1** was synthesized from 1-bromoadamantane via four reaction steps, as illustrated in Scheme 1 ($n = 0$). Yield of each reaction step was fairly high. 1-Phenyladamantane was prepared in 92% yield by the coupling reaction of 1-bromoadamantane and phenylmagnesium bromide in dichloromethane according to the procedure reported by Eguchi and co-workers.[13] It should be noted that the bromination of 1-phenyladamantane proceeded in a highly regioselective fashion to give 1-(4-bromophenyl)adamantane in a quantitative yield. The bulky adamantane substituent certainly induces the regioselective electrophilic aromatic substitution. On the other hand, 3-bromo-1,1′-biadamantane[14] ($n = 1$, Scheme 1) was a starting material for **2**. The synthesis of **2** sometimes suffered from the low solubility of both the starting materials and the products during the course of synthesis and isolation. However, the yields of products aimed at **2** were sufficiently high and comparable to the corresponding steps for **1**. Both solid monomers, **1** and **2**, were purified by flash column chromatography and by careful repeating recrystallizations prior to the anionic polymerization.

Anionic Polymerization of 1 and 2. The results of anionic polymerization of **1** and **2** are summarized in Table 1. Polymerizations of monomers were carried out with *sec*-butyllithium (*s*-BuLi), lithium naphthalenide, cumylpotassium, potassium naphthalenide, and oligo(α-methylstyryl)dipotassium in THF at −78 °C. The initiators included mono- and difunctional types, carbanions, and radical anions. When the monomer was added to the solution of initiator, the polymerization system always showed a characteristic yellow color in organolithium initiating system and a deep red color in organopotassium system. The colors attributed to polystyryl anions remained unchanged during the course of polymerization at −78 °C but disappeared instantaneously by quenching with a small amount of degassed methanol. The precipitated polymers were obtained by pouring the reaction mixture into large excess of methanol. Yields of polymers were quantitative in all cases.

The polymerization of **1** proceeded homogeneously at −78 °C. Complete consumption of **1** was achieved within 5 min by the initiation with *s*-BuLi (run 1). The size exclusion chromatography (SEC) curve of the resulting poly(**1**) always showed a symmetrical and unimodal shape, indicating the rapid initiation and the absence of side reactions. The polydispersity indices, M_w/M_n, were within 1.1, based on the calibration curve using polystyrene standards. However, the observed M_n values by the SEC with a simple refractive index (RI) detector were significantly lower than the calculated values based on the molar ratios between monomer to initiators. We now consider that the hydrodynamic volume of poly(**1**) possessing bulky adamantyl group is smaller than that of polystyrene standards. In fact, the M_n values measured by the RALLS−SEC connected with three RI, LS, and viscosity detectors were in good agreement with the calculated ones. The estimated *a* values of Mark−Houwink equation for poly(**1**) in THF at 30 °C were 0.48, indicating the rather small hydrodynamic volume.[15] This value was remarkably smaller than that of polystyrene, $a = 0.65$. We now believe that the M_n values by RALLS−SEC are reliable, while the relative M_ns are underestimated by the normal SEC measurement using polystyrene standards. Furthermore, the absolute M_n

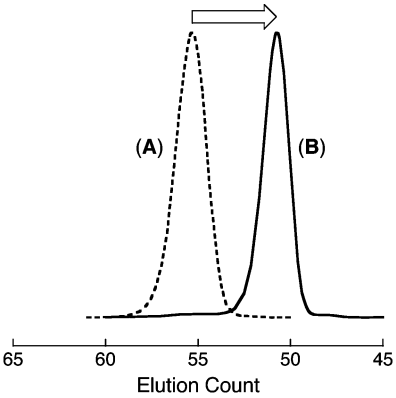


Figure 1. SEC curves of prepoly(**1**) (**A**) and postpoly(**1**) (**B**): peak **A**, M_n(calcd) = 4700, M_n(RALLS) = 4600, M_w/M_n = 1.04); peak **B**, M_n(calcd) = 15 000, M_n(RALLS) = 17 000, M_w/M_n = 1.06).

determination using vapor pressure osmometry (VPO) also supported that the resulting poly(**1**)s certainly possessed the predicted molecular weights (Table 1, run 2, M_nVPO = 5500; run 3, M_nVPO = 11 000; and run 5, M_nVPO = 25 000.). Thus, the M_n values could be controlled by the feed molar ratio of monomer to initiators ([M]/[I]) in the range of 4600−57 000. These results show that the polymerization of **1** proceeds in a controlled fashion to afford a polymer with well-defined chain structure under the conditions employed here.

We then tried the postpolymerization of **1** to prove the living nature of the polymerization system. The first-stage polymerization of **1** was performed with *s*-BuLi at −78 °C for 3 h. After complete consumption of the monomer, the resulting polymerization mixture was divided into two portions. One was terminated with methanol, while second-feed of **1** was added to the other one to further propagate the second-stage polymerization. Pre- and postpolymer were obtained quantitatively after the termination. Both SEC curves are unimodal and very narrow, as shown in Figure 1. The SEC curve of the postpolymer evidently shifts toward the higher molecular weight region from the elution count of prepolymer. The observed M_n values of the pre- and postpolymers agreed well with the predicted ones. These results substantiate that a stable anionic living polymer of **1** forms at −78 °C.

The anionic polymerization of **2** was next performed in THF under the highly diluted conditions (Experimental Section) because of the low solubility of **2** in THF even at room temperature. Although the polymerization proceeded homogeneously in several cases (runs 11−13, 17), off-white precipitate was formed in the reaction systems where the initial feed molar ratios [M]/[I] were more than 30 (runs 14−16). In these cases, the resulting polymer was precipitated within a few minutes after the addition of **2** to the initiator systems. Nevertheless, quantitative conversion of **2** was always attained at −78 °C after 4−16 h, even if the polymerization system was heterogeneous. In the homogeneous systems, the resulting poly(**2**)s had narrow molecular weight distributions and predicted molecular weights. However, significant deviations between the calculated M_n values and estimated ones were observed in the polymers obtained from the heterogeneous systems, whereas the molecular weight distributions were narrow. In summary, the resulting poly(**2**) of M_n value up to 13 000 shows good controls on M_n and M_w/M_n, indicating the living manner of polymerization of **2** as well as **1**.

Block and Random Copolymerization. The living character of the polymerization allows us to synthesize new well-defined block polymers containing thermally stable poly(**1**) and poly(**2**) segments. In addition, the results of the block copolymerization will provide the relative reactivity of new monomers and the propagating carbanions of resulting living polymers. Styrene and isoprene were used as comonomers for **1** or **2**, as shown in Table 2. The M_n values of block copolymers could be estimated from either RALLS−SEC or ^{1}H NMR measurements.

At first, the living polymers of **1** and **2** were employed as the macroinitiators for the sequential copolymerization with styrene or isoprene (runs 18, 20, and 22). In each case, the block copolymer with predicted composition and molecular weight was obtained quantitatively in THF at −78 °C. Figure 2 clearly shows the narrow molecular weight distribution of the resulting block copolymer derived from **2** and styrene. The SEC curve of poly(**2**)-*b*-polystyrene is symmetrical and unimodal, and completely shifts from that of homopolymer of **2** to higher molecular weight region after the addition of styrene. This is a clear evidence for the living character of propagating carbanion of poly(**2**) under the reaction conditions.

We next employed **1** or **2** as a second monomer to synthesize block copolymers with reversed sequences. Anionic living polymer of styrene or isoprene was prepared at the first-stage polymerization initiated with *s*-BuLi or potassium naphthalenide, respectively. The second-stage polymerizations of **1** and **2** smoothly proceeded in all cases to form a series of AB diblock and ABA triblock copolymers having tailored chain architectures.

The results obtained in the sequential copolymerizations indicate that crossover reactions between propagating anion of poly(**1**) or poly(**2**) and styrene take place rapidly to provide well-defined block copolymers, and vice versa. This means that monomer reactivities of **1**, **2**, and styrene and nucleophilicities of their living polymer are comparable to allow the quantitative crossover reaction. This is also supported by the results of homopolymerization of **1** and **2** performed with the various anionic initiators possessing different reactivity. We have previously reported that the anionic polymerizability of a series of 4-substituted styrenes is readily predictable from the ^{13}C NMR chemical shifts of β-carbons in the vinyl groups of monomers.[16] The β-carbon chemical shifts of **1**, **2**, and styrene are 113.1, 113.4, and 113.8 ppm, respectively. These comparable values also support that the anionic polymerizabilities of three styrene monomers are almost equal in accordance with the polymerization results.

We have thus speculated from the observed comparable anionic polymerizability that random cross-propagation between **1** and styrene is possible. We therefore attempted to synthesize the random copolymers of **1** with styrene as shown in Table 3. Mixtures of **1** and styrene in various molar ratios were polymerized with *s*-BuLi in THF at −78 °C. Total degree of polymerization of **1** and styrene was aimed to be around 100 in each polymerization to compare the thermal properties of copolymers. The ^{1}H NMR measurements of the reaction mixtures confirmed the complete consumptions of comonomers. As expected, the compositions of polymers were in accordance with the predicted ones based on the feed molar ratios of **1** and styrene. The resulting copolymers had symmetrical SEC curves, and the M_w/M_n values were within 1.03, indicating the extremely narrow molecular weight distributions. Moreover, there was a good agreement between calculated M_n values and those estimated by the SEC with triple detectors. We now consider that the random copolymerization of **1** and styrene has proceeded in a controlled manner.

Solubilities and Thermal Properties. Both polystyrenes bearing adamantyl and 1,1′-biadamantyl moieties were white powders. Poly(**1**) could be cast into transparent and brittle films

Table 2. Sequential Copolymerization of 1 and 2 with Styrene and Isoprene in THF at −78 °C[a]

				block copolymer (homopolymer[b])				
		monomer		$M_n \times 10^{-3}$				
run	initiator	first	second	calcd[c]	RALLS[d]	NMR[e]	M_w/M_n[f]	T_g, °C
18	*s*-BuLi	**1**	styrene	32 (22)	32	32	1.04	203, 108
19	*s*-BuLi	styrene	**1**	36 (11)	46	41	1.04	212, 104
20	cumyl-K	**1**	isoprene	41 (32)	42	39	1.06	216, −23
21	K−Naph	isoprene	**1**	37 (16)	40	44	1.09	199, −27
22	*s*-BuLi	**2**	styrene	21 (5.2)	26 (7.4)	26	1.04 (1.04)	202, 104
23	*s*-BuLi	styrene	**2**	18 (11)	22 (13)	23	1.04 (1.04)	204, 102
24	K−Naph	isoprene	**2**	45 (27)	47 (25)	45	1.09 (1.06)	211, −16

[a] Polymer yields were quantitative in all cases. Polymerization times were 3 h for **1** and **2**, 1 h for styrene, and 2 h for isoprene. [b] Homopolymers were obtained at the first-stage polymerization. [c] M_n(calcd.) = (MW of monomer) × [monomer]/[initiator] + MW of initiator residue. [d] M_n(RALLS) was obtained by RALLS−SEC using THF as an eluent. [e] M_n(NMR) was determined by using the molecular weight of the homopolymer and the molar ratio of monomer units in the block copolymer analyzed by ^{1}H NMR. [f] M_w/M_n were obtained by SEC caliblation using polystyrene standards in THF solution.

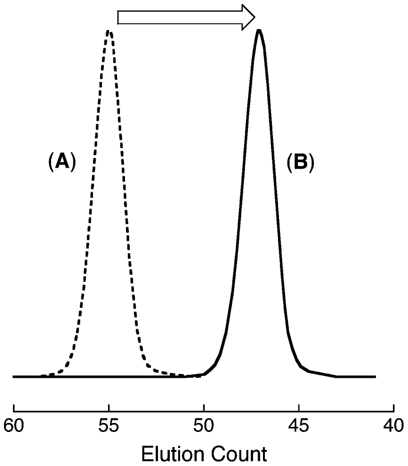


Figure 2. SEC curves of poly(**2**) (**A**) and poly(**2**-*b*-styrene) (**B**): peak **A**, M_n(calcd) = 5200, M_n(RALLS) = 7400, M_w/M_n = 1.04); peak **B**, M_n(calcd) = 21 000, M_n(RALLS) = 26 000, M_w/M_n = 1.04).

from the THF solution, while all the attempts of film formation from poly(**2**) solution failed. Table 4 shows the solubility of poly(**1**) and poly(**2**) obtained in this study along with that of polystyrene. Poly(**1**) and poly(**2**) exhibited the similar solubility in the various solvents, while their solubilities are relatively limited compared to polystyrene. They were soluble in cyclohexane, benzene, carbon tetrachloride, chloroform, and THF,[17] but were insoluble in solvents for polystyrene such as acetone, ethyl acetate, 1,4-dioxane, and *N*,*N*-dimethylformamide. Interestingly, poly(**1**) and poly(**2**) were readily soluble in cyclohexane even at ambient temperature, although polystyrene was barely soluble in cyclohexane, Θ solvent, above 40 °C. This is probably due to the high affinity of cyclohexane toward the lipophilic adamantyl and 1,1′-biadamantyl pendant groups in poly(**1**) and poly(**2**).

The T_g values of poly(**1**) and poly(**2**) were analyzed by differential scanning calorimetry (DSC), as shown in Table 1 and Figure 3. A reasonable dependence of T_g on the molecular weight was observed in each case similar to the case of polystyrene. The T_g values of poly(**1**) and poly(**2**) became almost constant at the high molecular weight region, and reached 234 and 232 °C, respectively. Those are almost 130 °C higher than the value of parent polystyrene ($T_g \sim 100$ °C). To our best knowledge, these observed T_gs are the highest values for alkyl-substituted polystyrene derivatives synthesized previously.[18] In each case, no melting transition was observed before the thermal degradation. These facts indicate that the incorporation of the bulky adamantyl or 1,1′-biadamantyl group induces the decreasing of chain mobility and the increasing of rotational barrier to result in the large T_g enhancement of polymers.

We next analyzed the T_g of block copolymers. In each case, two glass transitions were observed in the DSC curve as shown in Table 2. In the cases of diblock copolymers of **1** or **2** with styrene, two T_gs were detected around 102−108 and 202−212 °C. The lower one is T_g of polystyrene segment and the higher one is due to that of poly(**1**) or poly(**2**) segment. These DSC observations clearly indicate that these block copolymers containing polystyrene segment cause microphase separation in the bulk, as expected. Poly(**1**)-*b*-polyisoprene also shows two typical DSC peaks at +216 and −23 °C, corresponding to the T_g values of poly(**1**) and polyisoprene segments,[19] respectively. The triblock copolymer possessing outer hard poly(**1**) segments, poly(**1**)-*b*-polyisoprene-*b*-poly(**1**), similarly presented T_g values at +199 and −27 °C. On the other hand, two T_gs at +211 and −16 °C were observed for poly(**2**)-*b*-polyisoprene-*b*-poly(**2**). Although the microstructure of polyisoprene segments in these triblock copolymers mainly contains a 3,4-mode,[19] the observed T_g values are sufficiently low to act as the TPEs. We herein demonstrate a synthetic pathway of new TPEs showing very high service temperature (∼200 °C) derived from the high T_gs of poly(**1**) and poly(**2**) hard segments.

We then tried to control the T_g values of copolymer derived from **1** and styrene by changing the feed molar ratio of **1** and styrene in random copolymerization, as shown in Table 3. Only one glass transition behavior was observed in the DSC curve of each copolymer. Figure 4 shows the relationship between the observed T_g values and the observed composition of copolymer. The T_g increases with composition from 100 °C of polystyrene to 234 °C of poly(**1**) as predicted by the Fox equation.[20] The random copolymer obtained by the radical copolymerization of **1** with styrene also showed the T_g (164 °C) predictable from the composition. These results strongly indicate the random incorporation of **1** with styrene in the copolymer and the effective T_g controls tuned by the content of poly(**1**) repeating unit. In other words, the service temperature of hard segments in TPEs can be designed in the range of 100−234 °C by the feed molar ratio of **1** and styrene.

Thermal stability of the resulting polymers was finally investigated by thermogravimetric analysis (TGA) under nitrogen. Figure 5 shows the TGA thermograms of polystyrene, poly(**1**), and poly(**2**). There was not a significant difference in the initial decomposition temperatures of polymers. All the polystyrenes were stable until 340 °C, and then the thermal degradation of main chain started on heating. Small difference in 10% weight loss temperature (T_{10}) was observed in the TGA curves. Poly(**1**), poly(**2**), and polystyrene exhibited T_{10} at 406, 420, and 400 °C, respectively. When the residual weight of polystyrene was reduced to zero around 460 °C, poly(**1**) and poly(**2**) still maintained ca. 20 or 60% of residual weights,

Table 3. Random Copolymerization of 1 and Styrene in THF at −78 °C with *s*-BuLi[a]

			content (wt %) of **1**		$M_n \times 10^{-3}$				
run	initiator	DP[b]	calcd	obsd[c]	calcd[d]	RALLS[e]	M_w/M_n[f]	T_g, °C	T_{10},[g] °C
25	*s*-BuLi	103	0	0	11	10	1.04	91	398
26	*s*-BuLi	99	38	38	13	13	1.03	115	396
27	*s*-BuLi	114	71	71	19	20	1.03	170	396
28	*s*-BuLi	111	90	89	24	25	1.02	212	401
29	*s*-BuLi	108	100	100	26	26	1.03	234	398
30	AIBN[h]	-	70	74	-	12	1.77	164	-

[a] Polymer yields were quantitative in all cases. [b] Degree of polymerization = [**1**]/[initiator] + [styrene]/[initiator]. [c] Content (wt %) of **1** in copolymer was estimated from ^{1}H NMR. [d] M_n(calcd.) = (MW of monomer) × [monomer]/[initiator] + MW of initiator residue. [e] M_n(RALLS) was obtained by RALLS−SEC using THF as an eluent. [f] M_w/M_n was obtained by SEC caliblation using polystyrene standards in THF solution. [g] 10% Weight loss temperature in TGA curve. [h] **1** and styrene were polymerized with AIBN in benzene at 70 °C for 24 h.

Table 4. Solubility of Polymers[c]

solvent	poly(**1**)	poly(**2**)	polystyrene
n-hexane	I	I	I
cyclohexane	S	S	S[a]
benzene	S	S	S
CCl_4	S	S	S
$CHCl_3$	S	S	S
acetone	I	I	S
ethyl acetate	I	I	S
diethyl ether	I	I	I
1,4-dioxane	I	I	S
THF	S	S[b]	S
DMF	I	I	S
MeOH	I	I	I
H_2O	I	I	I

[a] Soluble above 40 °C. [b] Poly(**2**) with M_n higher than 40 000 was partially soluble in THF. [c] Key: S, soluble; I, insoluble.

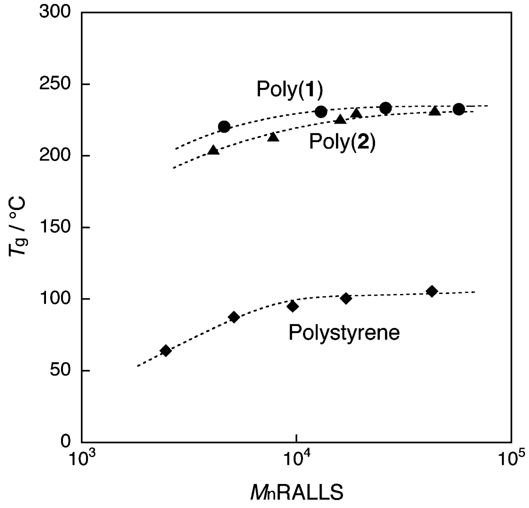


Figure 3. Relationship between M_n and T_g of poly(**1**) (●), poly(**2**) (▲), and polystyrene (◆).

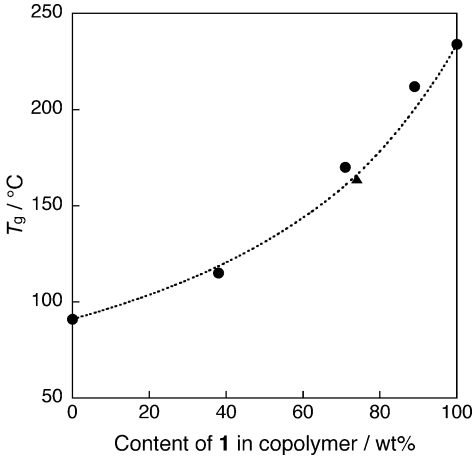


Figure 4. Relationship between T_g of poly(**1**-*ran*-styrene) (●, anionically polymerized; ▲, radically polymerized) and the weight composition with Fox prediction (broken line).

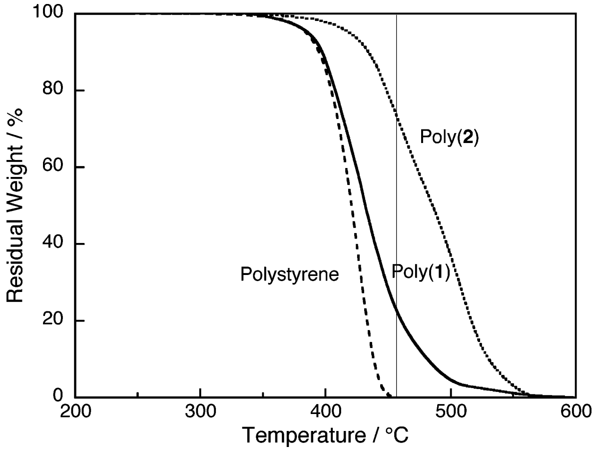


Figure 5. TGA thermograms of polymers under nitrogen flow with a heating rate of 10 °C min^{-1}.

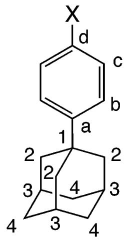
respectively. This clearly shows the heat-resistant property of adamantyl-substituted polystyrenes against the thermal degradation compared to polystyrene. We now consider that the main chain degradation is retarded by the introduced bulky and stiff adamantyl and 1,1-biadamantyl moieties on the side chain. The restricted chain mobility might play very important role to achieve these thermal stabilities of poly(**1**) and poly(**2**).

In conclusion, we have realized the living anionic polymerization of two newly designed styrene derivatives para-substituted with adamantyl and 1,1′-biadamantyl moieties, **1** and **2**. Polymerizations of **1** and **2** proceed smoothly to give the homopolymers with regulated chain lengths. A series of well-defined AB, BA, and ABA block copolymers are also obtained by the reversible sequential copolymerization of **1** or **2** with styrene or isoprene. The resulting poly(**1**) and poly(**2**) show a significantly high T_g values at 234 and 232 °C on the DSC thermograms. These high T_g values and the success of sequential block copolymerization of **1** and **2** with isoprene open the new synthetic pathway of TPEs showing high service temperatures. The incorporation of bulky and stiff adamantyl and 1,1′-biadamantyl moieties induces not only the significantly high T_gs but also the higher thermal stability of poly(**1**) and poly(**2**) on the TGA measurement.

Experimental Section

Materials. 1-Bromoadamantane was kindly supplied from Idemitsu Kosan Co. Ltd. 3-Bromo-1,1′-biadamantane was prepared according to our previous report.[12] Dichloromethane was distilled from CaH_2 under nitrogen. *N*,*N*-Dimethylformamide for monomer synthesis was purified by vacuum distillation from CaH_2. Diethyl ether was dried over sodium wire. Styrene was washed with 5% NaOH solution and with water, and then dried over anhydrous $MgSO_4$. It was then distilled over CaH_2 under vacuum. Isoprene was dried over CaH_2 and distilled on a vacuum line. *n*-Heptane was washed with concentrated H_2SO_4 and 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. Oligo(α-methylstyryl)lithium was freshly prepared prior to the polymerization from *s*-BuLi and 2−4-fold α-methylstyrene in THF at 20 °C for 1 min and then −78 °C for 10 min. Metal naphthalenides were prepared by the reactions of a small excess of naphthalene with the corresponding alkali metal in THF. Oligo(α-methylstyryl)dilithium and -dipotassium were prepared from the corresponding metal naphthalenides and 2−4-fold α-methylstyrene at 20 °C for 1 min and then −78 °C for 10 min. Cumylpotassium was prepared from cumyl methyl ether and potassium−sodium alloy in THF.[21] These initiators were sealed off under high vacuum conditions in ampules equipped with breakseals 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.[22]



X = H, Br, CHO, $CH{=}CH_2$

Synthesis of Monomers. 1-Phenyladamantane. A solution of bromobenzene (28.5 g, 182 mmol) in 100 mL of diethyl ether was added dropwise at room temperature to magnesium (7.22 g, 297 mmol) activated with 1,2-dibromoethane in diethyl ether (20 mL) under nitrogen. The reaction mixture was stirred at room temperature for 1 h. After completion of the reaction, the ether solution of Grignard reagent was moved to another flask to remove the residual magnesium. The Grignard reagent in ether was concentrated to give a solid in vacuo. 1-Bromoadamantane (12.9 g, 60.0 mmol) and 140 mL of dry dichloromethane was added to the solidified Grignard reagent under nitrogen, and then the mixture was refluxed for 24 h.[13] After the mixture was allowed to cool to room temperature, the reaction system was carefully poured into 2 N HCl at 0 °C and the layers were separated. The aqueous layer was extracted with dichloromethane three times. The combined organic layer was washed with water and dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, flash column chromatography (silica gel, hexane) gave white solid of 1-phenyladamantane (11.7 g, 55.2 mmol, 92%, mp = 84−85 °C (ref 8, mp = 89 °C)).

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.72-1.82$ (m, 6H, $C(2)H_2$), 1.92 (s, 6H, $C(4)H_2$), 2.10 (s, 3H, C(3)H), 7.15−7.20 (m, 1H, C(d)H), 7.29−7.39 (m, 4H, C(b)H and C(c)H).

^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 29.0$ (C3), 36.2 (C1), 36.9 (C2), 43.2 (C4), 124.9 (Cc), 125.6 (Cd), 128.2 (Cb), 151.4 (Ca).

IR (KBr): 2928, 2901, 2850, 1630, 1512, 1447, 1352, 989, 902, 845, 832, 809 cm^{-1}.

1-(4-Bromophenyl)adamantane. Bromine (50 mL, 0.97 mol) was added to the solution of 1-phenyladamantane (10.6 g, 50.0 mmol) in 100 mL of carbon tetrachloride and stirred for 4 h at room temperature. The reaction mixture was carefully poured into crashed ice, and excess bromine was treated with $NaHSO_3$ at 0 °C to separate the layers. The aqueous layer was extracted with chloroform three times. The combined organic phase was washed with water and dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by flash column chromatography (silica gel, hexane) to afford 1-(4-bromophenyl)adamantane (14.4 g, 49.6 mmol, 99%, mp = 101−102 °C (ref 8, mp = 101 °C)) as white solid.

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.71-1.81$ (m, 6H, $C(2)H_2$), 1.87 (s, 6H, $C(4)H_2$), 2.09 (s, 3H, C(3)H), 7.21−7.43 (4H, C(b)H and C(c)H).

^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 28.9$ (C3), 36.1 (C1), 36.7 (C2), 43.1 (C4), 119.3 (Cd), 126.9 (Cc), 131.1 (Cb), 150.4 (Ca).

IR (KBr): 2925, 2846, 1490, 1472, 1447, 1395, 1343, 1315, 1102, 1076, 1006 (Ar−Br), 977, 832, 801, 715 cm^{-1}.

4-(1-Adamantyl)benzaldehyde. A solution of 1-(4-bromophenyl)adamantane (32.6 g, 112 mmol) in 120 mL of dry THF was added dropwise at room temperature to magnesium (4.90 g, 202 mmol) activated with 1,2-dibromoethane in THF (40 mL) under nitrogen. The reaction mixture was refluxed for 2 h to achieve the complete conversion. Dry DMF (14 g, 200 mmol) was then added dropwise to the reaction system at 0 °C under nitrogen. The reaction mixture was stirred overnight at room temperature and quenched with 2 N HCl under cooling at 0 °C. After concentration in vacuo, the reaction system was extracted with dichloromethane three times. The organic layer was washed with water and then dried over anhydrous $MgSO_4$. After concentration of the solution, flash column chromatography (silica gel, hexane/EtOAc = 10/1 v/v) gave white solid of 4-(1-adamantyl)benzaldehyde (23.1 g, 96.3 mmol, 86%, mp = 103−104 °C (ref 8, mp = 67 °C)).

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.74-1.84$ (m, 6H, $C(2)H_2$), 1.94 (s, 6H, $C(4)H_2$), 2.13 (s, 3H, C(3)H), 7.52−7.85 (4H, C(b)H and C(c)H), 9.98 (s, 1H, CHO).

^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 28.8$ (C3), 36.7 (C2), 37.0 (C1), 42.9 (C4), 125.7 (Cc), 129.8 (Cb), 134.2 (Cd), 158.6 (Ca), 192.3 (CHO).

IR (KBr): 2904, 2845, 1697 (C═O), 1603, 1570, 1448, 1391, 1343, 1305, 1224, 1207, 1169, 1103, 1030, 1012, 861, 834, 803, 700 cm^{-1}.

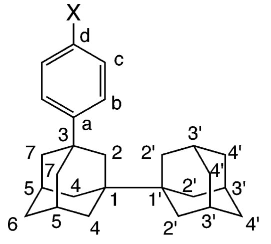
4-(1-Adamantyl)styrene (1). A mixture of potassium *tert*-butoxide (6.22 g, 55.4 mmol), methyltriphenylphosphonium bromide (14.0 g, 39.1 mmol), and dry THF (100 mL) was stirred for 20 min at room temperature under nitrogen. The mixture was cooled to 0 °C, and then a solution of 4-(1-adamantyl)benzaldehyde (8.11 g, 33.8 mmol) in 100 mL of dry THF was added dropwise. The mixture was stirred overnight at room temperature. The reaction was terminated with water and the layers were separated. The aqueous layer was extracted with diethyl ether three times, and the combined organic layer was dried over anhydrous $MgSO_4$. After concentration, the resulting yellow solid was dissolved in a small amount of THF, and the solution was poured into hexane to precipitate triphenylphosphine oxide. The precipitated triphenylphosphine oxide was removed by filtration, and the filtrate was concentrated in vacuo. The residual yellow solid was purified by flash column chromatography (silica gel, hexane) and by the following recrystallizations from hexane to give a white solid of **1** (6.21 g, 26.1 mmol, 77%, mp = 98−99 °C (ref 8, a colorless liquid)).

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.72-1.82$ (m, 6H, $C(2)H_2$), 1.91 (s, 6H, $C(4)H_2$), 2.10 (s, 3H, C(3)H), 5.17−5.21 (d, 1H, CH_2 = trans, $J = 11.1$ Hz), 5.68−5.74 (d, 1H, CH_2 = cis, $J = 17.7$ Hz), 6.65−6.75 (dd, 1H, ═CH trans, $J = 11.1$ and 17.7 Hz), 7.31−7.39 (4H, C(b)H and C(c)H).

^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 29.0$ (C3), 36.2 (C1), 36.9 (C2), 43.2 (C4), 113.1 (CH_2═), 125.1 (Cc), 126.0 (Cb), 135.0 (Cd), 136.7 (═CH), 151.2 (Ca).

IR (KBr): 2917, 2903, 2847, 1629 (C═C), 1510, 1446, 1405, 1345, 1103, 1038, 1011, 988, 897, 839, 808 cm^{-1}.

Anal. Calcd for $C_{18}H_{22}$ (238.37): C, 90.70; H, 9.30. Found: C, 90.50; H, 8.85.



X = H, Br, CHO, CH=CH$_2$

3-Phenyl-1,1′-biadamantane was prepared according to the similar procedure for 1-phenyladamantane by using bromobenzene (12.9 g, 81.6 mmol), magnesium (2.97 g, 122 mmol), and 3-bromo-1,1′-biadamantane[12] (6.96 g, 20.0 mmol). The reaction mixture of Grignard reagent and 3-bromo-1,1′-biadamantane was refluxed for 60 h to complete the reaction. Recrystallization of the crude product from hexane gave white solid of 3-phenyl-1,1′-biadamantane (6.51 g, 18.8 mmol, 94%, mp = 204−206 °C).

^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 1.53-1.70$ (m, 20H, C(2)H$_2$, C(6)H2, C(7)H$_2$, C(2′)H$_2$, C(4′)H$_2$), 1.83 (br s, 4H, C(4)H), 1.96 (br s, 3H, C(3′)H), 2.18 (br s, 2H, C(5)H), 7.15−7.20 (m, 1H, C(d)H), 7.30−7.39 (m, 4H, C(b)H and C(c)H).

^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 29.1$ (C3′), 29.6 (C5), 34.5 (C7), 35.4 (C2′), 36.5 (C1′), 36.7 (C2), 37.0 (C3), 37.60 (C1), 37.64 (C4′), 41.7 (C6), 42.8 (C4), 125.0 (Cc), 125.6 (Cd), 128.2 (Cb), 151.6 (Ca).

IR (KBr): 2928, 2849, 1599, 1495, 1446, 1345, 1312, 1103, 1078, 1024, 972, 769, 753, 726 cm^{-1}.

3-(4-Bromophenyl)-1,1′-biadamantane was prepared according to the similar procedure for 1-(4-bromophenyl)adamantane by using bromine (60 mL, 1.2 mol), 3-phenyl-1,1′-biadamantane (6.48 g, 18.7 mmol), and carbon tetrachloride (200 mL). Recrystallization of the crude product from hexane gave white solid of 3-(4-bromophenyl)-1,1′-biadamantane (6.50 g, 15.3 mmol, 82%, mp = 184−186 °C).

^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 1.60-1.70$ (m, 20H, C(2)H$_2$, C(6)H$_2$, C(7)H$_2$, C(2′)H$_2$, C(4′)H$_2$), 1.78−1.80 (br s, 4H, C(4)H), 1.96 (br s, 3H, C(3′)H), 2.17 (br s, 2H, C(5)H), 7.22−7.44 (4H, C(b)H and C(c)H).

^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 29.1$ (C3′), 29.6 (C5), 34.5 (C7), 35.4 (C2′), 36.5 (C1′), 36.7 (C2), 37.0 (C3), 37.55 (C1), 37.62 (C4′), 41.7 (C6), 42.8 (C4), 125.0 (Cc), 125.6 (Cd), 128.2 (Cb), 151.6 (Ca).

IR (KBr): 2917, 2903, 2849, 1491, 1474, 1448, 1395, 1344, 1009 (Ar−Br), 804, 733 cm^{-1}.

3-(4-Formylphenyl)-1,1′-biadamantane was prepared according to the similar procedure for 4-(1-adamantyl)benzaldehyde by using 3-(4-bromophenyl)-1,1′-biadamantane (6.24 g, 14.7 mmol), magnesium (0.83 g, 34.2 mmol), dry THF (135 mL), and dry DMF (6.63 g, 90.8 mmol). Flash column chromatography (silica gel, hexane/EtOAc = 10/1 v/v) of the crude product gave white solid of 3-(4-formylphenyl)-1,1′-biadamantane (3.21 g, 8.58 mmol, 58%, mp = 205−207 °C).

^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 1.56-1.69$ (m, 20H, C(2)H$_2$, C(6)H$_2$, C(7)H$_2$, C(2′)H$_2$, C(4′)H$_2$), 1.81−1.85 (br s, 4H, C(4)H), 1.97 (br s, 3H, C(3′)H), 2.21 (br s, 2H, C(5)H), 7.52−7.55 (4H, C(b)H and C(c)H), 9.98 (s, 1H, CHO).

^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 29.0$ (C3′), 29.4 (C5), 34.4 (C7), 35.4 (C2′), 36.5 (overlapped, C2, C1′), 37.5 (C4′), 37.6 (C3), 37.9 (C1), 41.3 (C6), 42.5 (C4), 125.8 (Cc), 134.2 (Cb), 134.2 (Ca), 158.9 (Cd). 192.2 (CHO).

IR (KBr): 2930, 2850, 1704 (C═O), 1604, 1572, 1448, 1345, 1310, 1221, 1208, 1175, 1103, 859, 829, 805, 720 cm^{-1}.

3-(4-Vinylphenyl)-1,1′-biadamantane (2) was prepared according to the similar procedure for **1** by using potassium *tert*-butoxide (1.56 g, 13.9 mmol), methyltriphenylphosphonium bromide (3.65 g, 10.0 mmol), dry THF (120 mL), and 3-(4-formylphenyl)-1,1′-biadamantane (3.18 g, 8.50 mmol). The resulting crude product was purified by flash column chromatography (silica gel, hexane). The following recrystallizations from hexane gave needle crystals of **2** (2.26 g, 6.08 mmol, 72%, mp = 170−172 °C).

^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 1.56-1.69$ (m, 20H, C(2)H$_2$, C(6)H$_2$, C(7)H$_2$, C(2′)H$_2$, C(4′)H$_2$), 1.81−1.85 (br s, 4H, C(4)H), 1.97 (br s, 3H, C(3′)H), 2.21 (br s, 2H, C(5)H), 5.17−5.21 (d, 1H, CH$_2$ = trans, $J = 10.9$ Hz), 5.68−5.73 (d, 1H, CH$_2$ = cis, $J = 17.6$ Hz), 6.65−6.75 (dd, 1H, ═CH trans, $J = 10.9$ and 17.6 Hz), 7.32−7.39 (4H, C(b)H and C(c)H).

^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 29.3$ (C3′), 29.5 (C5), 34.5 (C7), 35.4 (C2′), 36.5 (C1′), 36.7 (C2), 37.0 (C3), 37.57 (C4′), 37.61 (C1), 41.7 (C6), 42.7 (C4), 113.4 (CH$_2$═), 125.2 (Cc), 126.2 (Cb), 135.0 (Cd), 136.7 (═CH), 151.5 (Ca).

IR (KBr): 2928, 2850, 1630 (C═C), 1512, 1447,1403, 1345, 1312, 1103, 989, 901, 832, 809 cm^{-1}.

Anal. Calcd for $C_{28}H_{36}$ (372.59): C, 90.26; H, 9.74. Found: C, 90.01; H, 9.38.

Purification of Monomers. After careful recrystallizations of **1** and **2** from hexane, the purified monomers were dried over P_2O_5 for 24 h at ambient temperature in an apparatus equipped with a break-seal on a vacuum line and then diluted with dry THF. The resulting monomer solutions (0.2−0.4 M (0.048−0.095 g mL^{-1}) for **1** and 0.05−0.07 M (0.019−0.026 g mL^{-1}) for **2**, respectively) in THF were stored at −30 °C until ready to use for the anionic polymerization.

Anionic Polymerization. All anionic polymerizations were carried out in THF at −78 °C in an all-glass apparatus equipped with break-seals with vigorous shaking under high vacuum conditions (10^{-6} mmHg).[22] Polymerization was terminated with degassed methanol at −78 °C, and the reaction mixture was poured into methanol to precipitate a polymer. Polymers collected by filtration were purified by reprecipitations in THF/methanol system and by freeze-drying from their benzene solutions. Polymers thus obtained were characterized by ^{1}H and ^{13}C NMR, and IR spectroscopies. The following is the complete list.

Poly(1). ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 0.8-2.3$ (18H, CH$_2$-CH, C(2)H$_2$, C(3)H, C(4)H$_2$), 6.1−7.3 (4H, aromatic).

^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 29.1$ (C3), 35.9 (C1), 37.0 (C2), 40.0 (CH$_2$), 43.4 (CH, C4), 124.3 (Cc), 127.4 (Cb), 142.7 (Cd), 148.3 (Ca).

IR (KBr): 2925, 2847, 1511, 1449, 1344, 1318, 1102, 1015, 976, 833, 806 cm^{-1}.

Anal. Calcd for $(C_{18}H_{22})_n$: C, 90.70; H, 9.30. Found: C, 90.54; H, 9.39.

Poly(2). ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 0.8-2.3$ (32H, CH$_2$-CH, C(2)H$_2$, C(4)H$_2$, C(5)H, C(6)H$_2$, C(7)H$_2$, C(2′)H$_2$, C(3′)H, C(4′)H$_2$), 6.1−7.3 (4H, aromatic).

^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 29.0$ (C3′), 29.6 (C5), 34.6 (C7), 35.4 (C2′), 36.5 (C1′), 36.7 (C2), 36.8 (C3), 37.6 (C1, C4′), 40.0 (CH$_2$), 41.6 (C6), 43.0 (CH, C4), 124.6 (Cc), 127.5 (Cb), 143.5 (Cd), 148.7 (Ca).

IR (KBr): 2937, 2848, 1511, 1448, 1345, 1310, 1016, 973, 808 cm^{-1}.

Anal. Calcd for $(C_{28}H_{36})_n$: C, 90.26; H, 9.74. Found: C, 90.07; H, 9.93.

Radical Copolymerization. Radical copolymerization of **1** (0.295 g, 1.28 mmol) and styrene (0.133 g, 1.28 mmol) was performed with AIBN (0.016 g, 0.054 mmol) in benzene (5 mL) at 70 °C for 24 h. The reaction mixture was poured into methanol to precipitate a polymer (0.52 g, conversion∼100%). The copolymer collected by filtration was purified by reprecipitation in a THF/methanol system and by freeze-drying from the benzene solution.

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. 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 were determined by right angle laser light scattering size exclusion chromatography (RALLS−SEC) using an Asahi Techneion Viscotek Model 302 Triple Detector Array equipped with three polystyrene gel columns (TOSOH TSKgel $\mathrm{GMH_{HR}}$-H×2 and TSKgel $\mathrm{G2000H_{HR}}$) 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}. VPO measurements for number-average molecular weight determination were made with a Corona 117 instrument in benzene solution. The T_gs of the polymers were measured by DSC using a Seiko instrument DSC6220 apparatus under nitrogen flow. The polymer sample was first heated to 270 °C, cooled to 30 °C, and then scanned 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}.

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