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Synthesis and Properties of New Thermoplastic Elastomers Containing Poly[4-(1-adamantyl)styrene] Hard Segments

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ABSTRACT: The anionic polymerization of 4-(1-adamantyl)styrene (AdS) was carried out with *s*-BuLi in cyclohexane at 50 °C. The resulting poly(AdS) had predicted molecular weights, narrow molecular weight distributions, and high glass transition temperature (T_g) around 232 °C. A series of well-defined ABA type triblock copolymers, where B midblock stood for 1,4-polyisoprene and A end blocks for poly(AdS) (A), poly(AdS-*ran*-styrene) (AS), and polystyrene (S), were successfully synthesized by the sequential copolymerization with *s*-BuLi in cyclohexane. The 1,4-polyisoprene midblocks of triblock copolymers were completely converted into the saturated poly(ethylene-*alt*-propylene) (EP) blocks via hydrogenation with *p*-toluenesulfonhydrazide. Novel tailored thermoplastic elastomers, A−EP−A and AS−EP−AS, carrying bulky adamantyl groups in the hard end blocks were analyzed by dynamic mechanical analysis, stress relaxation test, tensile test, and transmission electron microscopy. These triblock copolymers were phase separated, and showed the high tensile strength (22−24 MPa), high elongation at break (590−660%), and high upper service temperature (175−210 °C). The heat resistant properties of A−EP−A and AS−EP−AS were drastically enhanced by substitution of the outer S segments in S−EP−S with either A or AS segments.

Introduction

Various thermoplastic elastomers (TPEs) such as polystyrene-*b*-polybutadiene-*b*-polystyrene (S−B−S), polystyrene-*b*-polyisoprene-*b*-polystyrene (S−I−S), and the corresponding hydrogenated triblock copolymers have been developed and widely used.[1] These ABA triblock copolymers are usually synthesized via the sequential anionic copolymerization of styrene and 1,3-dienes. The TPEs show the process ability under the melting conditions and the elasticity under the service conditions, which are typical for the thermoplastics and the vulcanized rubbers, respectively. The service conditions of conventional TPEs are often restricted by the glass transition temperature (T_g) of polystyrene blocks (100 °C), since the hard polystyrene end blocks act as a cross-linker under the T_g by forming the spheric or cylindorical microdomains separated in the continuous polydiene phase. To overcome this longstanding drawback, various efforts have been paid to increase the T_g of terminal hard segments in the TPEs. For example, poly(4-*tert*-butylstyrene)[2] and poly(α-methylstyrene)[3] displaying higher T_g values (130 and 165 °C, respectively) are employed to substitute polystyrene end blocks. However, the T_g value of the former one is not very attractive, and the synthesis of triblock copolymer is practically disturbed by the low ceiling temperature of the latter polymerization system.

It has been reported that the incorporations of bulky and rigid alicyclic substituents in the side chain are particularly effective to increase the T_g values of various parent polymers.[4–6] Among those substituents, adamantyl skeletons have been proved to demonstrate most drastic effect on T_g enhancement as well as the retardation of thermal degradation.[4,6]

We have recently succeeded in the living anionic polymerization of 4-(1-adamantyl)styrene (AdS) possessing a bulky, hydrophobic, and chemically and thermally stable adamantyl group.[7] The polymerizations of AdS smoothly proceed in THF at −78 °C to give the polymers with regulated chain lengths. Well-defined AB, BA, and ABA block copolymers are also obtained by the sequential copolymerization of AdS with styrene or isoprene by changing the additional order of comonomers. This strongly indicates that the anionic polymerizability of AdS is comparable to those conventional hydrocarbon monomers. More importantly, the resulting poly(AdS) shows a significantly high T_g value at 234 °C, indicating the enormous effect of purposefully introduced adamantyl skeleton to increase the T_gs of polymers.[7] Furthermore, the T_g values of random copolymers of AdS and styrene could be changed between 100 and 234 °C by tuning the feed molar ratio of comonomers. These significantly high T_g value and tunable nature on T_g are extremely attractive in order to synthesize new high performance TPEs in addition to the living character of the polymerization system of AdS. However, our previous report only deals with the anionic polymerization of AdS in a polar media of THF. It is well-known that the microstructure of polyisoprene produced in polar THF is a predominantly 3,4-mode not a 1,4-structure.[1] From the viewpoints of elasticity and heat resistant properties, 1,4-microstructure is highly desired for the polyisoprene midblock of TPEs.

Therefore, we herein attempt to anionically polymerize AdS in a typical nonpolar solvent of cyclohexane to examine the polymerizability. A series of tailored ABA triblock copolymers containing poly(AdS) and 1,4-polyisoprene segments are newly synthesized by the sequential copolymerization. After complete conversion of 1,4-polyisoprene midblock into poly(ethylene-*alt*-propylene) (EP) unit by the hydrogenation, the thermal and mechanical properties of the hydrogenated triblock copolymers are analyzed to demonstrate the effect of introduced adamantyl groups in the hard poly(AdS) terminal segments.

Results and Discussion

Anionic Polymerization of AdS in Cyclohexane. The results of anionic polymerization of AdS in cyclohexane are sum-

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Table 1. Anionic Polymerization of AdS with *s*-BuLi in Cyclohexane at 50 °C for 1 h[a]

run	*s*-BuLi (mmol)	AdS (mmol)	$M_n \times 10^{-3}$ calcd[b]	$M_n \times 10^{-3}$ RALLS[c]	M_w/M_n[d]	T_g[e] (°C)
1	0.0698	2.88	9.8	10	1.06	231
2	0.0347	3.39	23	24	1.04	232
3	0.0408	6.75	39	41	1.04	231

[a] Polymer yields were quantitative in all cases. [b] M_n(calcd) = (MW of monomer) × [monomer]/[*s*-BuLi] + MW of initiator residue. [c] M_n(RALLS) was obtained by RALLS−SEC using THF as an eluent. [d] M_w/M_n was obtained by SEC calibration using polystyrene standards in THF solution. [e] T_g was determined by DSC.

marized in Table 1. The polymerization of AdS was carried out with *sec*-butyllithium (*s*-BuLi) at 50 °C for 1 h. When AdS was added to the solution of *s*-BuLi, the color of polymerization system rapidly changed from colorless to characteristic orange. This orange color derived from propagating anion of poly(AdS) remained unchanged during the course of the polymerization but disappeared instantaneously on the addition of a small amount of degassed methanol. Complete consumptions of AdS were always achieved within 1 h, and yields of polymers were quantitative in all cases. The size exclusion chromatography (SEC) curves of poly(AdS)s were symmetrical and unimodal, and the polydispersity indices, M_w/M_n, were within 1.06, indicating the very narrow molecular weight distributions. The M_n values were controlled by the feed molar ratios of monomer to initiator. These results show that the polymerization of AdS in hydrocarbon also proceeds in a controlled fashion to afford a polymer with well-defined chain structures similar to the polymerizations in THF.[7] The differential scanning calorimetry (DSC) analysis of the resulting poly(AdS)s shows high T_g values around 230 °C similar to the T_gs of polymers obtained in THF at −78 °C.[7]

Random Copolymerization of AdS with Styrene in Cyclohexane. We have previously realized that the one-pot copolymerization of AdS with styrene in THF at −78 °C proceeds to give the random copolymer with well-defined chain structures.[7] The T_g values of those random copolymers could be varied from 100 to 234 °C by changing the content of AdS units in the copolymers. We herein attempted to synthesize the similar random copolymer of AdS and styrene in cyclohexane in order to tune the T_g.

An equimolar mixture of AdS and styrene was polymerized with *s*-BuLi in cyclohexane at 50 °C. The conversions of both monomers were monitored by ^{1}H NMR of the reaction mixtures. The copolymerization proceeded rapidly, and was completed after 30 min at 50 °C. The resulting copolymer possessed narrow molecular weight distribution and controlled M_n as well as the predicted composition. Figure 1 shows the time-conversion plot for the copolymerization of AdS with styrene in cyclohexane at 50 °C. The consumption rates of two comonomers are almost equal, indicating the comparable polymerizability of both monomers under the polymerization conditions. This means that random incorporation of AdS and styrene occurs during the course of the copolymerization. In fact, each resulting random copolymer showed a single glass transition at 180 °C, in the middle of T_gs of PS (100 °C) and of poly(AdS) (232 °C).

Synthesis of ABA Triblock Copolymers Containing Poly(AdS) Segments. In our preceding paper, we have synthesized a tailored ABA triblock copolymer, poly(AdS)-*b*-polyisoprene-*b*-poly(AdS), by the two-stage copolymerization initiated with potassium naphthalenide, a typical bifunctional initiator, in THF.[7] Since the first-stage polymerization of isoprene was performed in a polar solvent of THF, the resulting block copolymer mainly possessed 3,4- (57%) and 1,2- (33%) polyisoprene repeating units. The content of 1,4-microstructure was only 10%.

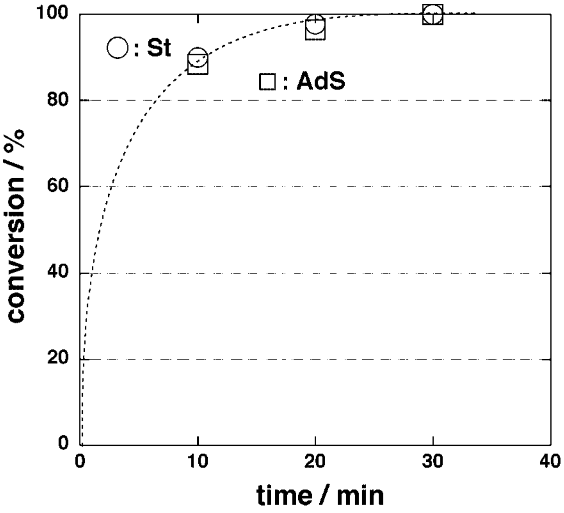

Figure 1. Time-conversion plot of copolymerization of AdS (50 mol %, □) and styrene (50 mol %, ○) with *s*-BuLi in cyclohexane at 50 °C.

In this paper, we attempt to synthesize two ABA type triblock copolymers possessing 1,4-polyisoprene midblock by the three-stage copolymerization of AdS and isoprene in cyclohexane, as shown in Scheme 1 and Table 2. The monomers of AdS, isoprene, and AdS were sequentially polymerized with *s*-BuLi at 50 °C (runs 4 and 5). After the first-stage polymerization of AdS for 1 h, isoprene as a second monomer was added to the resulting poly(AdS) anion. Then, the color of the polymerization system changed from orange to yellow. Polymerization of isoprene was performed for 3 h at 50 °C, and a second feed of AdS was then added to the polymerization system. The color of polymerization system slowly turned orange, indicating the formation of poly(AdS) propagating anion. A third-stage polymerization of AdS was terminated with methanol after 4 h reaction. Figure 2 shows the typical SEC curves of polymers obtained at each stage of polymerization (run 4). The SEC curves of diblock copolymer precursor and triblock copolymer completely shift toward higher molecular weight region from that of homopoly(AdS) with keeping the narrow molecular weight distribution. This is also a clear evidence for the living character of the polymerization of AdS in cyclohexane. The molecular weight of final block copolymer measured by the RALLS−SEC (M_n = 49 000) was in a good agreement with the calculated M_n value of 47 000. The content of hard poly(AdS) segments in the triblock copolymer estimated by ^{1}H NMR measurement was close to the calculated value as shown in Table 2. It is also noteworthy from the ^{1}H NMR measurement that the polyisoprene segment possesses predominantly 1,4-repeating unit (94%). This is almost consistent with the microstructure of polyisoprene obtained with *s*-BuLi in nonpolar hydrocarbons.[1] These results clearly show the formation of well-defined ABA triblock copolymer, poly(AdS)-*b*-polyisoprene-*b*-poly(AdS) (A−I−A).

In addition, we have synthesized a tailored ABA triblock copolymer possessing the outer hard A segments consisting of random copolymer of AdS and styrene (run 6). In this case, outer hard segments, poly(AdS-*ran*-styrene) (AS), were introduced by the random copolymerization of an equimolar mixture of AdS and styrene as described before. The contents of AdS and styrene units in the hard segment were regulated to 71 and 29 wt % to tune the T_g value of outer blocks. A conventional TPE, polystyrene-*b*-polyisoprene-*b*-polystyrene (S−I−S), was similarly synthesized by the sequential anionic copolymerization (run 7).

Scheme 1

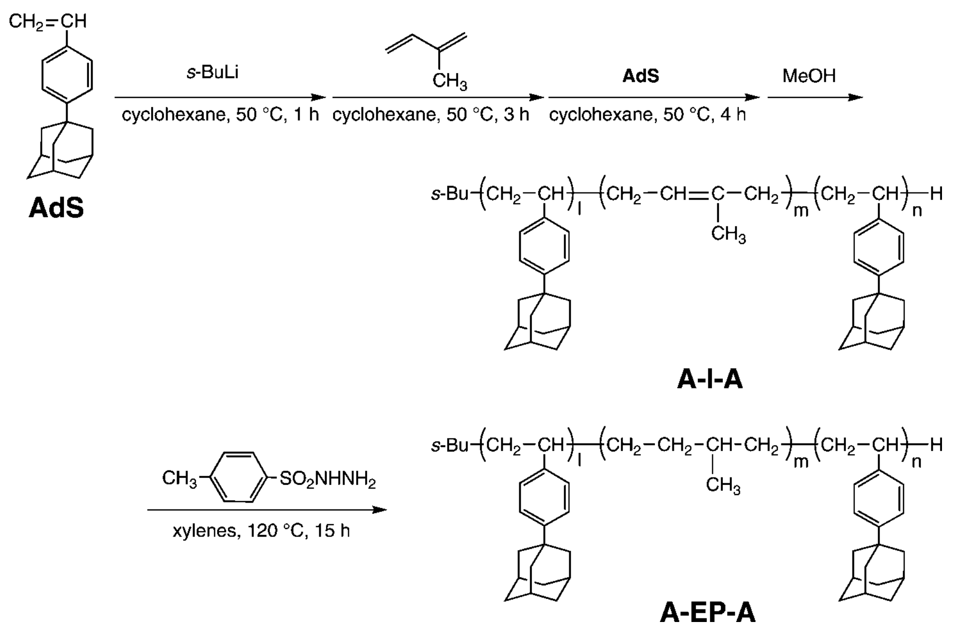

Table 2. Characterization of X−Polyisoprene−X Triblock Copolymers[a]

			$M_n \times 10^{-3}$		X composition (mol %)		X composition (wt %)		
run	sample	outer block X	calcd[b]	obsd[c]	calcd	obsd[d]	calcd	obsd[d]	M_w/M_n[c]
4	A−I−A-1	poly(AdS)	47 (9.7−25−12)	49[e]	20	19	46	45	1.12
5	A−I−A-2	poly(AdS)	80 (12−56−12)	78[e]	12	10	30	28	1.12
6	AS−I−AS	poly(AdS-*ran*-styrene)	74 (11−52−11)	80	14	11	30	25	1.03
7	S−I−S	polystyrene	31 (4.9−21−4.9)	44	23	22	32	30	1.04

[a] Yield ~ 100%. Polymerized with *s*-BuLi in cyclohexane at 50 °C. Polymerization time; AdS for 1 h; isoprene for 3 h. [b] M_n(calcd) = (MW of monomer) × [monomer]/[initiator] + MW of initiator residue. [c] M_n(obsd) and M_w/M_n were obtained by SEC calibration using polystyrene standards in THF solution. [d] X compositions (mol % and wt %) in copolymers were estimated from ^{1}H NMR. [e] M_n(obsd) was obtained by RALLS−SEC using THF as an eluent.

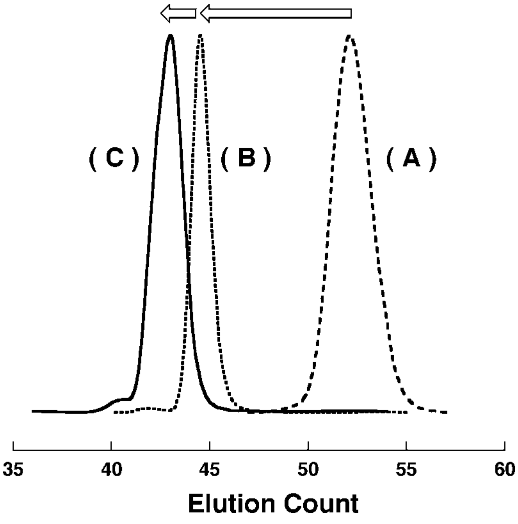

Figure 2. SEC curves of poly(AdS) (A), poly(AdS)-*b*-polyisoprene (B), and poly(AdS)-*b*-polyisoprene-*b*-poly(AdS) (C). Peak A: M_n(calcd) = 9700, M_n(RALLS) = 10 000, M_w/M_n = 1.06. Peak B: M_n(calcd) = 35 000, M_n(RALLS) = 37 000, M_w/M_n = 1.05. Peak C: M_n(calcd) = 47 000, M_n(RALLS) = 49 000, M_w/M_n = 1.12.

Hydrogenation of Block Copolymers. In order to increase the thermooxidation resistance, the unsaturated polyisoprene segment in a series of ABA triblock copolymers was hydrogenated with *p*-toluenesulfonhydrazide in xylenes at 120 °C for 15 h (Scheme 1).[8,9] The hydrogenated block polymers were characterized by ^{1}H NMR and SEC measurements. Figure 3 shows the typical ^{1}H NMR spectra of triblock copolymer, before and after the hydrogenation (run 4). Before hydrogenation, a signal corresponding to the −CH= proton of the predominant 1,4-structure of polyisoprene is observed at 5.1 ppm. Small two signals around 4.7 ppm also represent two CH_2= protons of the minor 3,4-structure of polyisoprene. After the hydrogenation, all these olefinic signals at 4.6−5.2 ppm disappear, and alternatively the signal intensity at 0.8−1.5 ppm increases. In the ^{13}C NMR spectrum, the signals corresponding to the olefin carbons at 131−132 ppm disappeared after the hydrogenation, and new signals were observed around 34 ppm. In addition,

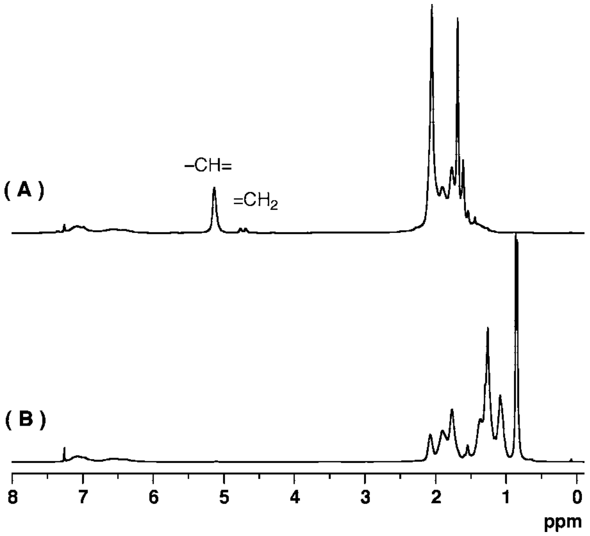

Figure 3. ^{1}H NMR spectra of poly(AdS)-*b*-polyisoprene-*b*-poly(AdS) before (A) and after hydrogenation (B) measured in $CDCl_3$.

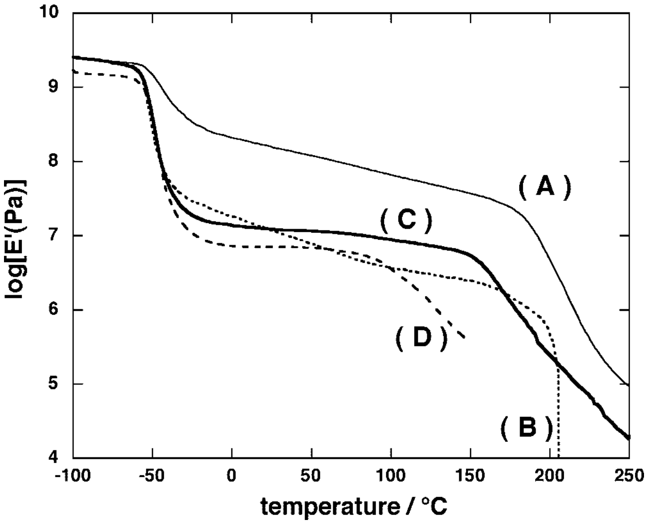

Figure 4. Temperature dependence of the tensile storage modulus (E') of block copolymers measured at 11 Hz frequency and heating rate of 3 °C min^{-1}: (A) A−EP−A-1, (B) A−EP−A-2, (C) AS−EP−AS, and (D) S−EP−S.

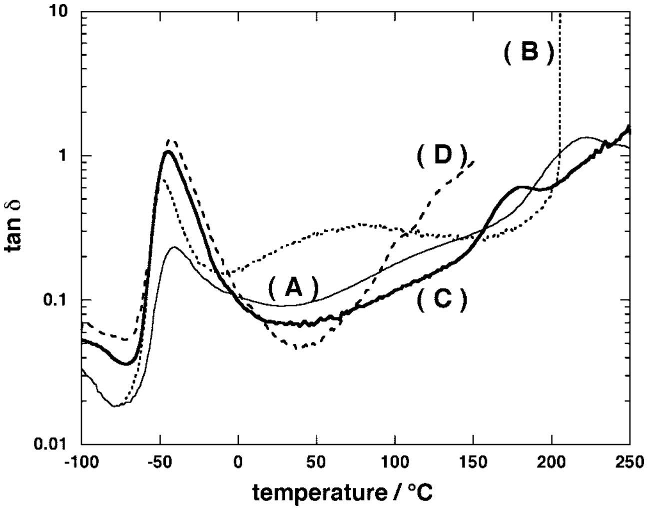

Figure 5. Temperature dependence of the loss factor (tan δ) of block copolymers measured at 11 Hz frequency and heating rate of 3 °C min^{-1}: (A) A−EP−A-1, (B) A−EP−A-2, (C) AS−EP−AS, and (D) S−EP−S.

the SEC curves of the hydrogenated block copolymers showed the unimodal and narrow shapes similar to those before the hydrogenation. We could thus conclude that the unsaturated polyisoprene segments in triblock copolymers were completely converted into the saturated ethylene-*alt*-propylene (EP) segments with keeping the well-defined primary chain structures. Therefore, the hydrogenated poly(AdS)-*b*-polyisoprene-*b*-poly(AdS) is designated as A−EP−A below.

Dynamic Mechanical Analysis (DMA). At first, we have measured the dynamic mechanical properties of the hydrogenated triblock copolymers having different hard segments such as poly(AdS), poly(AdS-*ran*-styrene), and polystyrene. The triblock copolymers are corresponding to A−EP−A, AS−EP−AS, and S−EP−S and possess the soft EP segment derived from the hydrogenated 1,4-polyisoprene block. Figures 4 and 5 show the thermal dependence of the tensile storage modulus (E') and the loss factor (tan δ) for the sheets of triblock copolymers in the temperature range from −100 to 250 °C at 11 Hz frequency.

In the DMA profiles, two clear transitions are observed, indicating that all the ABA triblock copolymers are phase separated. In each profile, the E' decreases from −60 °C because of the glass transition behavior for the soft EP midblock. As can be seen at higher temperature region in Figure 4, the comparable E' values in the rubbery plateau are observed for the triblock copolymers including A−EP−A-2, AS−EP−AS, and S−EP−S possessing similar hard block content (25−30 wt %). On the other hand, the E' value of A−EP−A-1 in the rubbery region is much higher than those of other three block copolymers. This is probably due to much higher hard block content (45 wt %) of A−EP−A-1 compared with other triblock copolymers. On heating of the sheet, the E' of S−EP−S started to decrease from 90 °C due to the glass transition of hard polystyrene segment, and the sheet was broken at 150 °C. On the other hand, the transitions from rubbery state to the viscous flow of other triblock copolymers containing AdS units occurred at higher temperatures. The E' values of AS−EP−AS, A−EP−A-2, and A−EP−A-1 decreased from 150, 170, and 180 °C, respectively. These softening temperatures are in good agreements with the contents of AdS units in the copolymers, as can be seen in Table 2. The sample sheets of AS−EP−AS and A−EP−A-1 were not broken even at 250 °C, while the A−EP−A-2 sheet largely deformed around 200 °C.

These observations were also confirmed in tan δ, as shown in Figure 5. In all profiles, the characteristic loss peaks of the soft EP midblocks clearly appeared between −40 and −50 °C. A significant difference in tan δ was realized at temperature higher than 100 °C. The loss peak for polystyrene end blocks of S−EP−S was very weak but was present at 100 °C, while a corresponding peak was observed around 175 °C for the poly(AdS-*ran*-styrene) end blocks of AS−EP−AS. These values are corresponding to the T_gs of the hard end blocks in the ABA triblock copolymers. On the other hand, a broad peak of α-relaxation of poly(AdS) end blocks appeared 220 °C for A−EP−A-1, while A−EP−A-2 did not show the corresponding transition in the DMA measurement. It should be noted that A−EP−A-1 certainly exhibited the two-stage glass transition behaviors at −58 and +214 °C in the DSC measurement, corresponding to the T_g values of EP and poly(AdS) segments. However, A−EP−A-2 only showed a single T_g at −60 °C for EP segment in the DSC measurement, although the phase separated morphology of A−EP−A-2 was observed as discussed later. Thus, the comparison of DMA data strongly indicates that incorporation of AdS units into the hard terminal segments significantly increases the service temperature of TPEs.

Stress Relaxation Behavior. Next, stress relaxation experiments of a series of triblock copolymers were performed at 100% jump uniaxial tensile strain at 40 °C. Figure 6 shows the stress relaxation behavior of the normalized stress values, $F(t)/F(20\ \mathrm{s})$, with a logarithmic time scale. All the samples gradually released the stress with time. Among four samples, A−EP−A-2 showed the most rapid stress relaxation, while the sample sheet was not broken within 7000 s. Although S−EP−S and A−EP−A-1 showed the comparable stress relaxation behaviors until 300 s, the specimen of S−EP−S was suddenly broken after 1400 s. It is noteworthy that S−EP−S and A−EP−A-1 possess similar degrees of polymerization of end blocks and midblock, while the weight fraction of hard segments of A−EP−A-1 (45 wt %) is significantly higher than that of S−EP−S (30 wt %). This clearly indicates the substitution effect of adamantyl groups to the phenyl rings of S−EP−S on the enhancement of mechanical property. On the other hand, AS−EP−AS exhibited the slowest stress relaxation behavior, and the sheet specimen was also intact over a time scale of employed conditions. According to the time−temperature superposition principle, the slow stress relaxation observing in

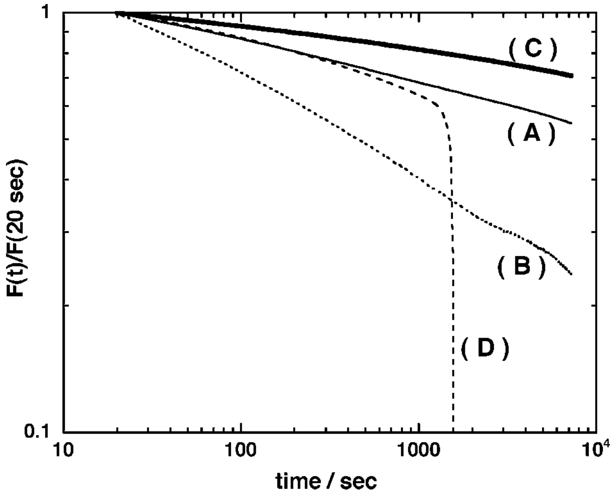

Figure 6. Stress relaxation behavior (F(t)/F(20 s)) of block copolymers measured at 40 °C: (A) A−EP−A-1, (B) A−EP−A-2, (C) AS−EP−AS, and (D) S−EP−S.

the experiment corresponds to the relaxation occurring at higher temperature and vice versa. From this viewpoint, the stress relaxation properties were improved in the samples possessing AdS monomer units in the hard end blocks, although A−EP−A-2 showed the most rapid relaxation as discussed below.

Morphological Observations. It is well-known that the equilibrium phase morphology of binary block copolymers is mainly controlled by their composition.[1] The morphology of triblock copolymers was analyzed by transmission electron microscopy (TEM) to further confirm the phase separation. The films of triblock copolymers were prepared by casting from the toluene solution, and were dried at 50 °C under vacuum. The TEM observation clearly supports the microphase separated structures of triblock copolymers as well as the DMA analyses. Figure 7 shows the cross-section TEM images of ultrathin films for three polymer samples containing AdS unit in the hard segments. The phases containing poly(AdS) and polystyrene units were observed as the dark phase, since the selective staining of film was carried out with RuO_4.

In the case of AS−EP−AS (Figure 7A), a cylindrical morphology is clearly observed. The cylinder domain is poly(AdS-*ran*-styrene) hard segment (25 wt %) and the continuous phase is soft EP domain (75 wt %), which is reasonable from the composition of block copolymer.[10] On the other hand, the morphologies of two A−EP−A samples are obscure and difficult to categorize. Considering the composition of A−EP−A samples, a plausible morphology of A−EP−A-1 (45 wt % of hard segment) should be lamellar without long-range order or cylinder (Figure 7B), and A−EP−A-2 (28 wt % of hard segment, Figure 7C) might form a "strut type" bicontinuous morphology as previously reported.[11] It is also noteworthy that the observed domain sizes in Figure 7 roughly agree with the total molecular weights of the triblock copolymers.

From the observed morphology in the TEM measurements, we speculated the reason why the physical properties of A−EP−A-2 sheet were disappointedly weak compared with other block copolymers. A possible explanation is that the rather high affinity of lipophilic adamantyl groups to hydrogenated EP midblock blurs the interface of separated phase.[12] This effect might weaken the immiscibility between poly(AdS) domain and EP domain and induce the obscure phase separation.[13] In other words, the introduced aliphatic adamantyl groups in poly(AdS) segment weakened the sharp phase separation and even induced the mixed poly(AdS)/EP phase because of the preferable affinity toward the EP domain. In fact, a broad maximum in tan δ was observed between 0 and 120 °C in Figure 5B (A−EP−A-2) presumably due to the mixed poly(Ad)/EP phase. A single T_g observed at −60 °C in the DSC measurement also supports the obscure phase separation of A−EP−A-2 sample as described before. On the other hand, A−EP−A-1 showed a similar unclear phase separation in Figure 7B. This might be also supported by the continuous decreasing of the E' value in the rubber plateau in the DMA measurement of A−EP−A-1 sample (Figure 4A) similar to the case of A−EP−A-2 (Figure 4B). Consequently, the most effective and preferable improvement of physical properties was attained in the AS−EP−AS sample not in the A−EP−A samples, since the partial substitution (~50 mol %) of aromatic rings in the polystyrene segment with adamantyl groups retained the sharp phase separation (Figure 7A) and induced the sufficiently high T_g of AdS containing hard segments (T_g = 175 °C, Figure 5).

Stress−Strain Behavior. Finally, we analyzed the mechanical properties of block copolymers by measuring the stress−strain curves of the hydrogenated triblock copolymers, as summarized in Table 3. Low initial modulus, high ultimate tensile strength, and high elongation at break were clearly observed for A−EP−A-1,[14] AS−EP−AS, and S−EP−S samples, as expected. These features of triblock copolymers are typical for the TPEs as well as the cross-linked rubber. The results indicate that the effective physical cross-linking occurs in the phase separation states of these block copolymers.

Figure 8 shows the typical stress−strain curves of tensile test for the hydrogenated triblock copolymers of A−EP−A-2, AS−EP−AS, and S−EP−S measured at room temperature and at a strain rate of 500 mm/min. The good mechanical property of AS−EP−AS was clearly demonstrated similar to S−EP−S as the conventional TPE. The values of ultimate tensile strength and elongation at break were rather improved in the case of AS−EP−AS. Poly(AdS-*ran*-styrene) segment plays very important roles to prevent the viscous flow of soft EP segments in the phase separated states of AS−EP−AS sample and to provide rubberlike properties at temperature below the T_g (175 °C) of hard AS domain as well as the polystyrene segment (T_g = 100 °C) in S−EP−S. By contrast, A−EP−A-2 showed an only high elongation at break, while the ultimate tensile strength was disappointingly low. The stress of the sheet was almost constant during the course of the elongation. It is indicative that the unclear phase separation (Figure 4B and Figure 7C) fails to cross-link physically to restrict the movement of EP domain even at room temperature. The composition of ABA triblock copolymer is essential for the preferable design of the high performance TPE. In addition, we should have an attention to the content of the introduced adamantyl groups, since the adamantyl skeletons in AdS unit might diminish the sharpness of the phase separation due to the high affinity toward the aliphatic EP segment.

Conclusions

We have succeeded in the living anionic polymerization of AdS initiated with *s*-BuLi in nonpolar solvent of cyclohexane similar to the polymerization in polar solvent such as THF. The success of living polymerization of AdS in nonpolar solvent allows us to synthesize a series of new ABA type triblock copolymers containing poly(AdS) terminal segments and 1,4-polyisoprene midblock via the sequential copolymerization. 1,4-Polyisoprene segments are converted into saturated EP segments by the quantitative hydrogenation. We have tuned the T_g of the end blocks in S−EP−S type TPEs by substituting the hard end blocks with either poly(AdS) or random copolymer segment containing AdS and styrene units. In fact, the hydrogenated triblock copolymers containing AdS unit clearly show higher T_gs (175−220 °C) than that of S−EP−S (T_g = 100 °C) on DMA

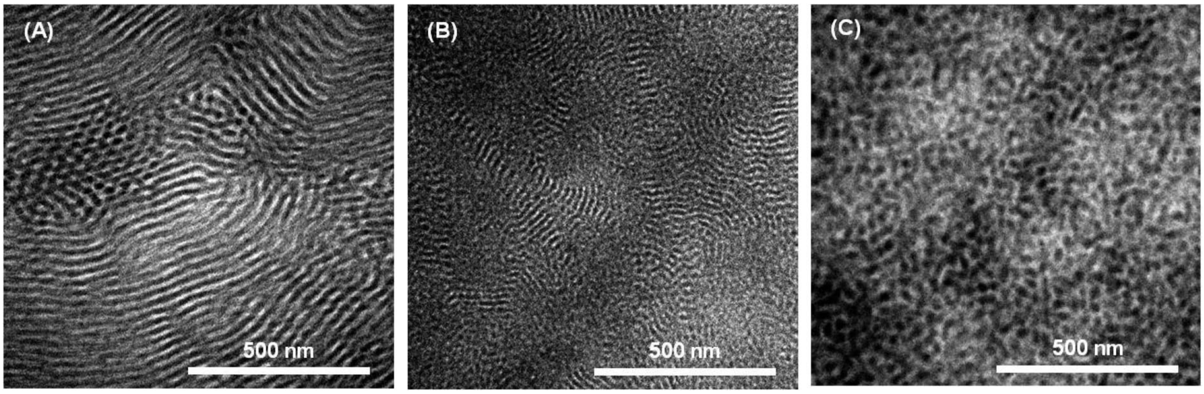

Figure 7. Transmission electron micrographs of AS−EP−AS (A), A−EP−A-1 (B), and A−EP−A-2 (C). Poly(AdS) and polystyrene were the dark phases stained with RuO_4.

Table 3. Mechanical Properties of Hydrogenated Triblock Copolymers Obtained from Stress−Strain Curves[a]

sample	wt % of hard segment	stress at 100% (MPa)	stress at 300% (MPa)	ultimate tensile strength (MPa)	elongation at break (%)
A−EP−A-1[b]	45	3.2	3.6	22.3 ± 4	590 ± 100
A−EP−A-2	28	1.5	1.5	3.3 ± 1	1100 ± 300
AS−EP−AS	25	2.1	3.5	23.9 ± 4	660 ± 100
S−EP−S	30	3.1	8.6	19.1 ± 3	540 ± 100

[a] Elongation rate = 500 mm min^{-1}. [b] Elongation rate = 40 mm min^{-1}.

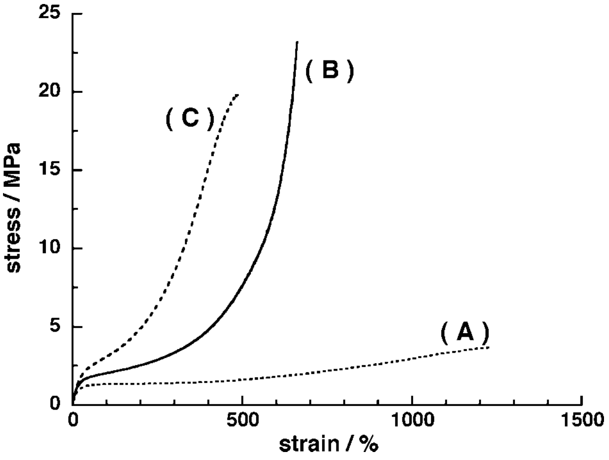

Figure 8. Stress−strain curves of triblock copolymers measured at room temperature: (A) A−EP−A-2, (B) AS−EP−AS, and (C) S−EP−S.

measurement in addition to the low T_g of EP segment (−50 °C). The resulting triblock copolymers exhibit various morphologies in TEM analysis as a result of microphase separation. High ultimate tensile strength and high elongation at break typical for the TPEs are achieved in the samples with clear microphase separation. Heat resistant properties of A−EP−A and AS−EP−AS are effectively enhanced by the introduction of adamantyl groups into the end blocks of novel TPEs. Thus, from the synthetic viewpoint, high service temperatures of new TPEs are realized by the living anionic polymerization of AdS in hydrocarbon.

Experimental Section

Materials. 4-(1-Adamantyl)styrene (AdS) was synthesized as previously reported.[7] Styrene was washed with 5% NaOH aqueous solution and with water and then was dried over anhydrous $MgSO_4$. It was then distilled over CaH_2 under vacuum. Isoprene was dried over CaH_2 and distilled. Cyclohexane was washed with concentrated H_2SO_4 and dried over anhydrous $MgSO_4$, and then dried over P_2O_5 for 1 day under reflux. It was then distilled in the presence of *n*-BuLi under nitrogen. *s*-BuLi in cyclohexane (1.3 M) was diluted with cyclohexane and used for the polymerization. Other commercially available reagents were used without further purification.

Anionic Polymerization. The polymerization was carried out in an all-glass apparatus equipped with breakseals under high vacuum conditions as previously reported.[15] In a typical experiment, a cyclohexane solution of *s*-BuLi (0.05 M, 0.0698 mmol) was added to a cyclohexane solution (20 mL) of AdS (0.69 g, 2.88 mmol) at room temperature. The polymerization system showed a characteristic orange color attributed to the poly(AdS) anion. The mixture was heated to 50 °C with stirring and reacted for 1 h. The reaction was then terminated with small amount of degassed methanol, and the reaction mixture was poured into MeOH to precipitate a polymer. The precipitated polymer (100%, M_n = 10,000, M_w/M_n = 1.06, T_g = 231 °C) was collected by the filtration.

Block Copolymerization. The sequential copolymerization was carried out either under high vacuum conditions or under nitrogen atmosphere. In a typical procedure under nitrogen, a dried glass reaction vessel equipped with rubber septum was charged with a cyclohexane solution of *s*-BuLi (0.05 M, 0.0807 mmol) and AdS (0.78 g, 3.28 mmol) in cyclohexane (15 mL) at room temperature, and the mixture was heated to 50 °C. After 1 h, a small portion of the reaction mixture was sampled and terminated with methanol. Isoprene (2.01 g, 29.5 mmol) in cyclohexane (15 mL) was then added to the reaction mixture. The polymerization of isoprene was performed at 50 °C for 3 h. A small portion of reaction mixture was sampled again, and finally AdS (0.71 g, 2.99 mmol) in cyclohexane (15 mL) was added. The third-stage polymerization of AdS was carried out at 50 °C for 4 h, and terminated with methanol. The mixture was poured into methanol to precipitate a block copolymer (100%).

Hydrogenation. A dried glass flask was charged with 2.50 g of poly(AdS)-*b*-polyisoprene-*b*-poly(AdS) (M_n = 49,000, 22.5 mmol of double bond), 20 g of *p*-toluenesulfonhydrazide (108 mmol, 4.8 equivalent per double bond), 150 mL of xylenes, and 30 mg of antioxidant (3,5-di-*tert*-butyl-4-hydroxytoluene). The mixture was refluxed at 120 °C for 15 h under nitrogen. The reaction system was cooled to room temperature and poured into a large excess of methanol to precipitate the polymer. The polymer (2.46 g, 98%) collected by filtration was further purified by reprecipitations in toluene/methanol system and dried in vacuo at 50 °C. Almost quantitative hydrogenation of the olefin functionalities was confirmed by ^1H (Figure 3B) and ^{13}C NMR of the resulting polymer (M_n = 49,000, M_w/M_n = 1.12, T_g = −58 and +214 °C). The conversion of the hydrogenation was higher than 98%.

Measurements. ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX300 spectrometer (300 MHz for ^1H 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 of 2×10^3 to 4×10^6) with either ultraviolet (254 nm) 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 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}. T_g values of the polymers were measured by DSC using a Seiko instrument DSC6220 apparatus under nitrogen. The polymer sample was first heated to 270 °C, cooled to −100 °C, and then scanned at a rate of 10 °C min^{-1}. Dynamic mechanical analysis (DMA) and stress relaxation test were carried out with a DVE-V4FT Rheospectoler (Rheology Co., Ltd.). Samples (20 × 5 × 1 mm) were cut from the heat-pressed sheet of block copolymer. In the DMA measurement, samples were deformed in tensile mode at a constant 11 Hz frequency at the heating rate of 3 °C min^{-1}. In stress relaxation test, 100% sudden strain was applied to the samples at 40 °C, and tensile stress, F(t), was recorded after 20 s of the stretching. Tensile measurements were conducted according to JIS-K6251 with a TM-MS-134 tensile tester (Instron Japan Co., Ltd.). The test pieces were extended at either at 40 mm min^{-1} or 500 mm min^{-1} at room temperature. Transmission electron microscopy (TEM) was measured by a Hitachi H-7100FA with an accelerating voltage of 100 kV. The block copolymers were cast from toluene solution and dried for a week at room temperature. The cast film was further dried at 50 °C for 20 h under vacuum. Then, the toluene-cast films were microtomed and stained with RuO$_4$ for 3−10 min.

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(9) Hahn, S. F. *J. Polym. Sci., Part A. Polym. Chem.* **1992**, *30*, 397–408. It is reported that the hydrogenation of 1,4-polyisoprene with *p*-toluenesulfonhydrazide in the presence of tri-*n*-propylamine in *o*-xylene only proceeded with in 68% conversion at reflux temperature for 4 h. In the present study, we have succeeded in the completion of the hydrogenation of the 1,4-polyisoprene segments in the block copolymers after 15 h without tri-*n*-propylamine in the presence of small amount of 3,5-di-*tert*-butyl-4-hydroxytoluene.

(10) In the cases of styrene−diene copolymers, a spherical morphology is reported for polystyrene contents up to 17 wt %. When the polystyrene content is in the range of 17−38 wt %, a cylindrical morphology is observed, whereas a lamellar morphology is reported for 36−62 wt % polystyrene content. (a) Gallot, B. R. M. *Adv. Polym. Sci.* **1978**, *29*, 85–156. (b) Tong, J. D.; Leclére, Ph.; Rasmont, A.; Brédas, J. L.; Lazzaroni, R.; Jérôme, R. *Macromol. Chem. Phys.* **2000**, *201*, 1250–1258.

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(12) A rather high lipophilic nature of poly(AdS) compared with polystyrene was suggested, since poly(AdS) was readily soluble in cyclohexane, which is a typical Θ solvent for polystyrene.

(13) We measured a DSC curve of a mixture of poly(AdS) and hydrogenated 1,4-polyisoprene (EP). Only the T_g of latter polymer was observed at −64 °C, whereas the T_g of poly(AdS) could not be detected similar to the case of A−EP−A-2. It is suggested that poly(AdS) and EP are not completely miscible.

(14) A yield point was observed in the stress-strain measurements for A−EP−A-1, although the elongation rate (40 mm/min) was different from other samples shown in Figure 8. This is probably due to the continuous morphology such as lamellar without long range order or cylinder (Figure 7B) as discussed by the TEM measurement. Yield point was not observed in the stress-strain curves for A−EP−A-2, AS−EP−AS, and S−EP−S as shown in Figure 8. In particular, A−EP−A-2 having a "strut type" bicontinuous morphology did not show a yield point, while the tensile strength was very low and almost constant during the elongation.

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