

Synthesis of Polystyrene-*b*-Poly(ethylene-*co*-butene) Block Copolymers by Anionic Living Polymerization and Subsequent Noncatalytic Hydrogenation

Guo-Dong Liang, Jun-Ting Xu, Zhi-Qiang Fan

Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China

Received 25 October 2005; accepted 20 December 2005

DOI 10.1002/app.24037

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A series of polystyrene-*b*-polybutadiene (PSt-*b*-PBd) block copolymers with various chain lengths and compositions were synthesized by sequential living anionic polymerization and then converted into the corresponding polystyrene-*b*-poly(ethylene-*co*-butene) (PSt-*b*-PEB) block copolymers through the selective hydrogenation of unsaturated polybutadiene segments. Noncatalytic hydrogenation was carried out with diimide as the hydrogen source. The microstructures of PSt-*b*-PBd and PSt-*b*-PEB were investigated with gel permea-

tion chromatography, ¹H-NMR, ¹³C-NMR, Fourier transform infrared, and differential scanning calorimetry. The results showed that the hydrogenation reaction was conducted successfully and that the chain length and molecular weight distribution were not altered by hydrogenation. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 2632–2638, 2006

Key words: block copolymers; polybutadiene; polystyrene; synthesis

INTRODUCTION

Block copolymers based on polybutadiene are widely used as thermoplastic elastomers, as compatibilizers of polymeric blends, and as impact-tough modifiers because of their good elastic properties and their special chain structure.¹ However, a disadvantage of these materials is their poor aging behavior, which is caused by the oxidation of residual double bonds in the polybutadiene, resulting in deterioration of the properties of these copolymers.² The chemical modification of butadiene-based polymers by hydrogenation is one of the most effective methods for improving stability against thermal, oxidative, and radiation-induced degradation of polymers.

Catalytic hydrogenation by gaseous hydrogen with transition-metal (e.g., Ru,³ Rh,^{4–6} Co,⁷ Ti,⁸ Pd,⁹ or Pt^{10,11}) compounds as a catalyst is widely used for the hydrogenation of polybutadiene-based copolymers. For example, RuCl₂(PPh₃)₃ and RhCl(PPh₃)₃ have been found to be suitable catalyst systems for the hydrogenation of polybutadiene³ and polybuta-

diene-based copolymers,^{4–6} respectively. In addition, a metallocene catalyst system has been found to be active for the hydrogenation of polybutadiene-based copolymers.^{8,12–15} However, catalytic hydrogenations of polybutadiene-based copolymers by gaseous hydrogen are usually carried out at high pressures and at high temperatures, which are very dangerous. Moreover, the catalysts used for hydrogenation are expensive and difficult to synthesize, and the ultimate products are usually stained by the colored catalysts.

An alternative hydrogenation method for polybutadiene-based copolymers is noncatalytic hydrogenation with diimide, which is based on the reaction between olefinic bonds (in both branching chains and backbone chains) and diimide.^{16–18} Podesva and Holler¹⁹ reported that almost full saturation of the double bonds in polybutadiene was achieved with diimide. Diimide is an unstable compound that can be generated *in situ* by the thermal decomposition of *p*-toluenesulfonylhydrazide (TSH).^{19–22} This greatly facilitates the hydrogenation process in comparison with the conventional catalytic hydrogenation method.

In this study, a series of polystyrene-*b*-polybutadiene (PSt-*b*-PBd) block copolymers were synthesized by the sequential living anionic polymerization of styrene and butadiene monomers. The polybutadiene block was hydrogenated by a noncatalytic method with diimide. Our focus was on the structural characterization of the block polymers before and after hydrogenation to investigate the effect of hydrogenation by such a method on the microstructure.

Correspondence to: J.-T. Xu (xujt@zju.edu.cn).

Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 20374046.

Contract grant sponsor: Excellent Young Teachers Program.

Contract grant sponsor: New Century Supporting Program for the Talents of the Ministry of Education.

EXPERIMENTAL

Materials

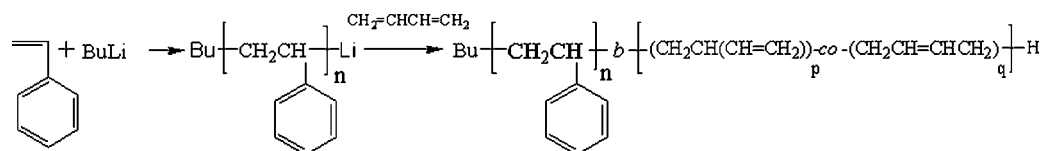
The monomer styrene (AP-grade) [analytical purity] was purchased from Hangzhou Chemical Co., Ltd. (Hangzhou, China). Styrene was washed with a 10% NaOH aqueous solution to remove the chemical inhibitor. After it was dried by calcium chloride over 48 h, styrene was distilled under reduced pressure over CaH₂ and stored in a refrigerator. Styrene was again distilled freshly under reduced pressure over CaH₂ before polymerization. The monomer butadiene was received as a technical product from Yangzi Petrochemical Co., Ltd. (Yangzi, China). Butadiene was evaporated from the container before each run, dried by passage through a column packed with molecular sieves, and dissolved into freshly distilled cyclohexane. Cyclohexane (AP-grade) was purchased from Hangzhou Chemical and refluxed in the presence of a Na/Ka alloy over argon. Cyclohexane was freshly distilled before use. A solution of *n*-BuLi in hexane (2.5M), purchased from Acros (Beijing, China), was used without further purification. Xylene, antioxidant 1010, and TSH were purchased from Hangzhou Chemical and were used as received.

Polymerization procedure

All the operations were conducted under dry and high-vacuum conditions. The sequential anionic polymerization of the styrene and butadiene monomers was conducted in a 150-mL Schlenk bottle with a magnetic stirrer. *n*-BuLi was used as the initiator, and cyclohexane was used as the solvent. The Schlenk bottle was washed with *n*-BuLi and rinsed with cyclohexane before the polymerization. The polymerization of styrene was carried out at 50°C for 3 h. After the polymerization of styrene, a certain amount of a butadiene/cyclohexane solution was added to the system at room temperature. The system was held for 30 min, and the temperature was raised to 50°C. The polymerization of butadiene lasted for 3 h and was terminated by the addition of methanol and precipitated by ethanol. A white solid or milklike liquid was collected by the removal of methanol and ethanol. The sequential polymerization of the styrene and butadiene monomers is illustrated in Scheme 1.

Hydrogenation of the PSt-*b*-PBd block copolymers

The hydrogenation of the PSt-*b*-PBd block copolymers was carried out in a three-necked glass reactor (150 mL)



Scheme 1 Sequential anionic polymerization of styrene and butadiene monomers.

equipped with a mechanical stirrer, a refluxing condenser, and a three-way stopcock for the inlet or outlet of inert gas. The PSt-*b*-PBd block copolymer and antioxidant 1010 (0.1 w/v %) were dissolved in xylene, and the solution was stirred and heated under an argon atmosphere up to approximately 100°C. TSH was added rapidly to this hot solution. With continuous stirring under argon, the mixture was heated and refluxed for 7 h and then was poured into ethanol. A white solid was collected by filtration. The white solid was purified by extraction with boiling methanol in a Soxhlet extractor. The remaining solid was dried in a vacuum oven at 80°C overnight. Scheme 2 shows schematically the hydrogenation of the PSt-*b*-PBd block copolymers by TSH.

Gel permeation chromatography (GPC)

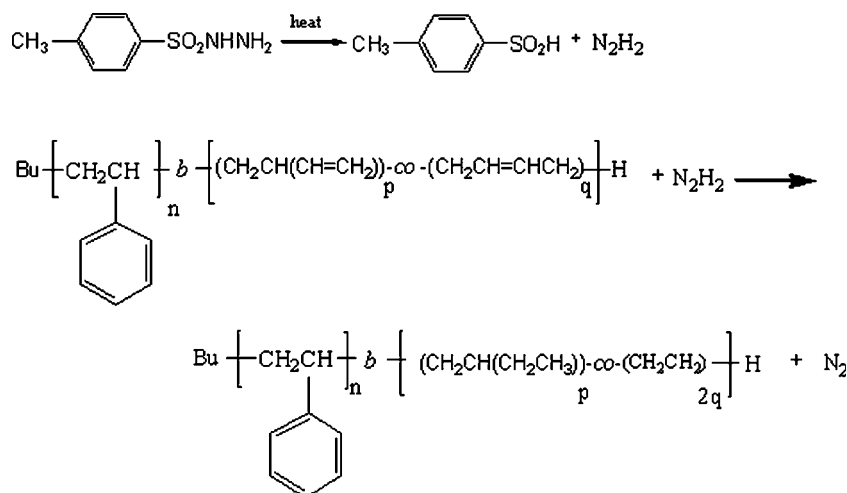
The molecular weight distribution of the PSt-*b*-PBd block copolymers was performed on a Waters (Milford, MA) 150C gel permeation chromatograph at room temperature with tetrahydrofuran (THF) as the solvent and a Waters R403 differential refractometer. GPC of the polystyrene-*b*-poly(ethylene-*co*-butene) (PSt-*b*-PEB) block copolymers was conducted in a PL 220 GPC instrument (Polymer Laboratories, Ltd., Amherst, MA) at 150°C in 1,2,4-trichlorobenzene. The number-average molecular weight (M_n) was reported with polystyrene (PSt) standards.

NMR

¹H-NMR spectra of the PSt-*b*-PBd block copolymers were obtained with a Bruker (Rheinstetten, Germany) AMX-500 NMR spectrometer. The samples were analyzed in a deuterated chloroform solution at room temperature. The chemical shifts were recorded in parts per million and referenced to tetramethylsilane as the internal standard. ¹H and ¹³C-NMR spectra of the PSt-*b*-PEB block copolymers were also obtained with a Bruker AMX-500 NMR spectrometer. The samples were analyzed in a deuterated dichlorobenzene solution at 120°C.

Fourier transform infrared (FTIR)

FTIR analysis was carried out with a PerkinElmer (Boston, MA) model 16PC spectrometer. Thin-film samples ~10 μm thick were prepared by the pressing of PSt-*b*-PEB block copolymer pellets between two polytetrafluoroethylene (PTFE) films. After the com-



Scheme 2 Hydrogenation of PSt-*b*-PBd block copolymers.

plete melting of the pellets, the molten materials were pressed into thin films and cooled to room temperature. Finally, the thin-film samples were peeled from the PTFE films. For PSt-*b*-PBd block copolymers, a PSt-*b*-PBd/THF dilute solution was cast onto a KBr disk, and the solvent was allowed to evaporate under reduced pressure before the test.

Differential scanning calorimetry (DSC)

Cooling and heating scans of the PSt-*b*-PBd and PSt-*b*-PEB block copolymers were conducted with a PerkinElmer Pyris-1 differential scanning calorimeter under a nitrogen atmosphere. The PSt-*b*-PEB block copolymers (ca. 10 mg) were sealed in aluminum pans and held at 180°C for 5 min to eliminate the thermal history. They were then cooled to -50°C at a cooling rate of 10°C/min, and this was followed by a heating process to 180°C at a rate of 10°C/min. The cooling scans and the following heating scans were recorded.

RESULTS AND DISCUSSION

PSt-*b*-PBd block copolymers with various chain lengths and compositions were synthesized by the sequential anionic living polymerization of styrene and butadiene monomers. Selective hydrogenation was carried out by the treatment of these samples with TSH in refluxing toluene. This selective hydrogenation converted the PSt-*b*-PBd block copolymers into the corresponding PSt-*b*-PEB block copolymers.

The M_n and molecular weight distribution values of the PSt-*b*-PBd block copolymers were determined by GPC and are summarized in Table I. All the PSt-*b*-PBd block copolymers exhibited a single, narrow GPC peak, and the polydispersity index varied between 1.08 and 1.16 for all PSt-*b*-PBd block copolymers, indicating clearly that block copolymers, instead of blends of the corresponding homopolymers, had formed.

¹H-NMR experiments were carried out to determine the composition and polymerization degrees of styrene (n) and butadiene ($m = p + q$) for the PSt-*b*-PBd block copolymers (where p and q are the polymerization degrees of butadiene units with 1,2-addition and 1,4-addition, respectively). Figure 1(a) shows a representative ¹H-NMR curve of the PSt-*b*-PBd block copolymers. The monomer composition of the sample was determined from the integrals of the following ¹H resonances (δ , ppm, CDCl₃, 25°C): 7.07 and 6.56 (aromatic protons in styrene units), 5.38 (unsaturated protons in butadiene units of 1,4-addition), 4.96 (unsaturated end protons in butadiene units of 1,2-addition), and 0.8 (protons of the methyl end group from the initiator), which are denoted b , d , e , and a , respectively, as shown in Figure 1(a). The molar ratio of styrene units to butadiene units in the PSt-*b*-PBd block copolymers (R_S) was calculated as follows:

$$R_S = n/(p + q) = \frac{I_b/5}{(I_d + I_e)/2} \quad (1)$$

where I_b , I_d , and I_e are the intensities of proton resonances b , d , and e , respectively. The molar fraction of 1,2-addition in total butadiene units ($X_{1,2}$) was determined by

$$X_{1,2} = p/(p + q) = I_e/(I_d + I_e) \quad (2)$$

$X_{1,2}$ was ~ 5 mol % for all the PSt-*b*-PBd block copolymers. The value of $X_{1,2}$ was strongly dependent on the initiator, solvent, polymerization temperature, and so-called structure modifiers.²³ Tsiang and coworkers²⁴⁻²⁶ investigated the effects of structure modifiers, such as THF and ethers, on the preparation of the styrene-butadiene-styrene triblock copolymer. They reported that $X_{1,2}$ could be tuned in the range of 10–89 mol % by the selection of the proper structure modifier and concentration. Sierra et al.²⁷ prepared a polystyrene-*b*-poly

TABLE I
Characteristics of PSt-*b*-PBd and Corresponding PSt-*b*-PEB Block Copolymers

Sample	PSt- <i>b</i> -PBd					PSt- <i>b</i> -PEB					
	$M_n (\times 10^{-3})^a$	M_w/M_n	R_S^b	$X_{1,2}^c$	$S_n B_m^d$	Sample	R_1^e	W_E^f	V_E^f	X_{ethyl}^g	$S_n E_x^h$
1	20.3	1.16	19.85	0.042	$S_{198}B_{11}$	1h	9.43	0.028	0.035	0.022	$S_{199}E_{20}$
2	22.4	1.12	4.18	0.049	$S_{202}B_{50}$	2h	2.04	0.121	0.148	0.024	$S_{201}E_{96}$
3	23.4	1.11	3.25	0.053	$S_{200}B_{65}$	3h	1.54	0.156	0.190	0.023	$S_{202}E_{124}$
4	27.6	1.08	0.88	0.056	$S_{198}B_{226}$	4h	0.44	0.434	0.492	0.026	$S_{199}E_{452}$
5	40.8	1.11	1.25	0.048	$S_{280}B_{224}$	5h	0.62	0.334	0.387	0.025	$S_{282}E_{451}$
6	15.6	1.09	0.26	0.058	$S_{57}B_{225}$	6h	0.13	0.870	0.894	0.026	$S_{59}E_{453}$
7	7.4	1.12	0.84	0.045	$S_{66}B_{79}$	7h	0.42	0.448	0.506	0.023	$S_{65}E_{155}$
8	24.6	1.09	0.87	0.051	$S_{155}B_{180}$	8h	0.43	0.439	0.497	0.024	$S_{156}E_{358}$

^a Determined by GPC at room temperature.

^b Calculated from ¹H-NMR curves of PSt-*b*-PBd block copolymers (see the text).

^c Calculated with eq. (2).

^d Subscripts n and m are the polymerization degrees of styrene and butadiene blocks in PSt-*b*-PBd, respectively, calculated with eqs. (3) and (4) (see the text).

^e Calculated from the ¹H-NMR curves of PSt-*b*-PEB block copolymers.

^f W_E and V_E are the weight and volume fractions of the PEB block in PSt-*b*-PEB block copolymers, respectively, and are calculated as follows: $W_E = 28x/(28x + 104n)$ and $V_E = 1/[1 + (1/W_E - 1)d_E/d_S]$, where d_E and d_S are the densities of branching of polyethylene and PSt at 120°C (0.801 and 1.01 g/cm³, respectively).²⁸

^g Calculated with eq. (8).

^h Subscripts n and x are the polymerization degrees of styrene and ethylene blocks in PSt-*b*-PEB, respectively, calculated with eqs. (6) and (7) (see the text).

(ethylene-*co*-butylene)-*b*-polystyrene triblock copolymer by anionic polymerization. They reported that the values of $X_{1,2}$ varied between 7.6 and 44.9 mol %. Pispas et al.⁶ prepared polybutadiene-*b*-poly(*tert*-butyl methacrylate) block copolymers in benzene with *sec*-BuLi as the initiator. They reported about 8 mol % 1,2-addition in total polybutadiene units.

The average n and m values for the PSt-*b*-PBd block copolymers were determined by the comparison of the resonance intensities of styrene and butadiene units with that of the methyl end group with the following equations:

$$n = (I_b/5)/(I_a/3) \quad (3)$$

$$m = p + q = [(I_d + I_e)/2]/(I_a/3), \quad (4)$$

where I_a , I_b , I_d and I_e are the intensities of corresponding peaks in Figure 1(a). The *cis*-diimide, produced by the *in situ* thermal decomposition of TSH, reduced the unsaturated butadiene units of 1,4-addition and 1,2-addition into polyethylene segments with ethyl branches, whereas the aromatic groups of the styrene segment were intact.²⁰ Figure 1(b) shows a representative ¹H-NMR curve of PSt-*b*-PEB block copolymers reduced from the corresponding PSt-*b*-PBd block copolymers. The unsaturated vinyl proton resonances disappeared completely after the hydrogenation of PSt-*b*-PBd block copolymers, indicating that the hydro-

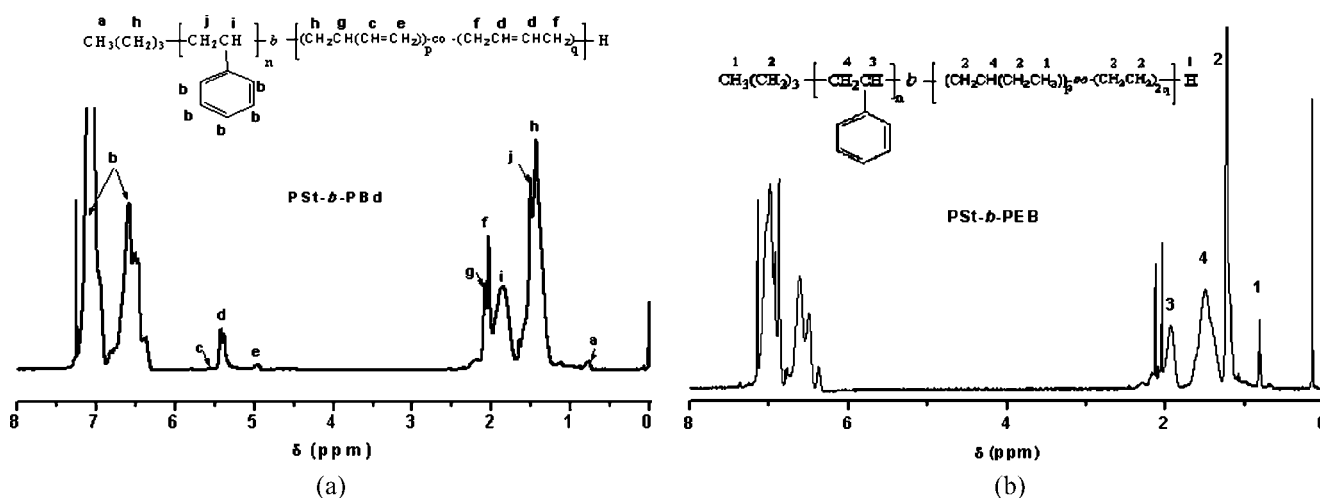


Figure 1 ¹H-NMR spectra of (a) the PSt-*b*-PBd block copolymer and (b) the corresponding PSt-*b*-PEB block copolymer.

generation reaction was quantitative. The molar ratio of styrene units to ethylene units in the PSt-*b*-PEB block copolymers (R_1) was calculated from $^1\text{H-NMR}$ curves of PSt-*b*-PEB block copolymers by the comparison of the integrals of the following ^1H resonances (δ , ppm, $\text{C}_6\text{D}_4\text{Cl}_2$, 120°C): 1.5 (protons of methylene in styrene units and methine in 1-butene units), 1.95 (proton of methine in styrene units), 1.23 (protons of methylene from hydrogenated butadiene units and from the initiator), and 0.81 (protons of the end groups from the initiator and hydrogenated butadiene units), which are denoted 4, 3, 2, and 1, respectively, as shown in Figure 1(b).²⁰ With one hydrogenated butadiene unit of 1,2-addition viewed as two ethylene units, R_1 could be evaluated by

$$R_1 = n/(2p + 2q) \\ = I_3/\{[I_2 - 4(I_4 - 2I_3)]/4 + 2(I_4 - 2I_3)\}, \quad (5)$$

where $[I_2 - 4(I_4 - 2I_3)]/4 + 2(I_4 - 2I_3)$ is the total intensity of ethylene units (where I_1 , I_2 , I_3 and I_4 are the intensities of the corresponding peaks in Figure 1(b). The polymerization degrees of styrene and ethylene units (n and $x = 2p + 2q$) in the PSt-*b*-PEB block copolymers were calculated as follows:

$$n = I_3/(I_{\text{CH}_3}/6) \quad (6)$$

$$x = 2p + 2q \\ = \{[I_2 - 4(I_4 - 2I_3)]/4 + 2(I_4 - 2I_3)\}/(I_{\text{CH}_3}/6) \quad (7)$$

where $I_{\text{CH}_3} = I_1 - 3(I_4 - 2I_3)$ is the intensity of end methyl groups, instead of branching methyl groups, in the PSt-*b*-PEB block copolymers.

The molar percentage of ethyl branches in the polyethylene segment (X_{ethyl}) of the PSt-*b*-PEB block copolymers was determined with the following equation:

$$X_{\text{ethyl}} = p/(2p + 2q) \\ = 2(I_4 - 2I_3)/\{[I_2 - 4(I_4 - 2I_3)]/4 + 2(I_4 - 2I_3)\} \quad (8)$$

The data of R_s , n , m , and $X_{1,2}$ for the PSt-*b*-PBd block copolymers and R_1 , n , m , and X_{ethyl} for the PSt-*b*-PEB block copolymers are summarized in Table I. R_1 , calculated from $^1\text{H-NMR}$, was very close to half of R_s . Comparing the n values in PSt-*b*-PBd and corresponding PSt-*b*-PEB, we can see that the chain length of PSt remained almost unchanged after hydrogenation. On the other hand, x in PSt-*b*-PEB was nearly twice m in corresponding PSt-*b*-PBd, indicating that hydrogenation did not alter the chain length of the PBd segment either. Moreover, X_{ethyl} was about 2.5 mol % for all PSt-*b*-PEB block copolymers, which was half of the molar percentage of butadiene units from 1,2-addition in the PSt-*b*-PBd block copolymers.

Because the crystalline poly(ethylene-*co*-butene) (PEB) block was insoluble in THF after hydrogenation, high-temperature GPC was used to characterize the molecular weight distribution of the PSt-*b*-PEB block copolymers, employing trichlorobenzene as the solvent. Figure 2 shows high-temperature GPC curves of samples 2 (before hydrogenation) and 2h (after hydrogenation) in Table I. No significant difference in the retention time was observed before and after hydrogenation, and this showed that selective hydrogenation of the PSt-*b*-PBd block copolymers had little effect on the molecular weight distributions of the block copolymers.

All the data showed that hydrogenation saturated only the double bonds in butadiene units, whereas the microstructure of the block copolymers, including the chain lengths of two blocks, the concentration of branches, and molecular weight distribution, remained intact. As a result, we can conclude that the hydrogenation reaction from PSt-*b*-PBd to corresponding PSt-*b*-PEB was carried out quantitatively, and side reactions arising from the addition of bis(*p*-tolyl)disulfide and its precursor, *p*-toluenesulfonic acid, to the residual olefinic double bonds of the polybutadiene block during the hydrogenation could be ignored.¹⁹

$^{13}\text{C-NMR}$, FTIR, and DSC were used to verify further the chain structure of the PSt-*b*-PEB block copolymers. Figure 3 shows the aliphatic region of the $^{13}\text{C-NMR}$ spectrum of the PSt-*b*-PEB block copolymer, and the assignment of the $^{13}\text{C-NMR}$ spectrum is inserted in the figure. The peak at $\delta = 41.2$ ppm denotes the long, continuous styrene sequence (SSSS).²⁰ The hydrogenated polybutadiene block can be viewed as a copolymer of ethylene (E) with a small amount of 1-butene (B). The main peak at $\delta = 29.8$ ppm results from the long ethylene sequence (EEEE). The peaks at δ values of 9.5, 33.9, 26.5, and 10.9 ppm were assigned to an EEBEE sequence. The absence of peaks at δ values of 30.1, 31.6, 27.6, 37.3, and 43.8 ppm, which were produced by

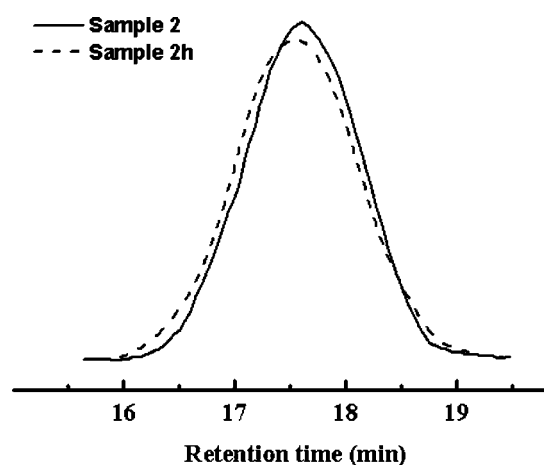


Figure 2 Representative high-temperature GPC curves of PSt-*b*-PBd and corresponding PSt-*b*-PEB block copolymers.

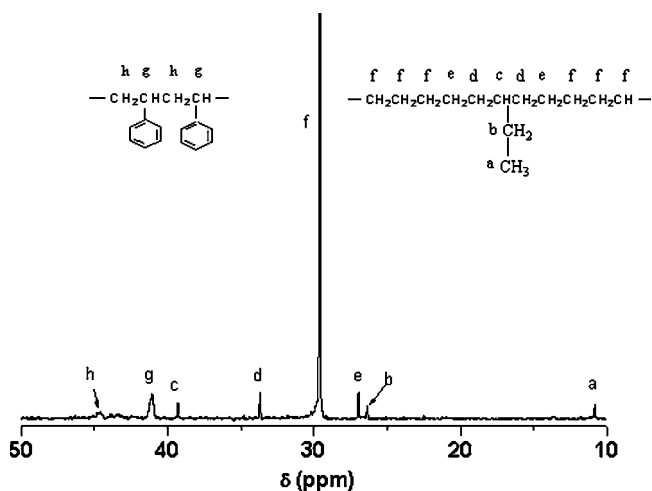


Figure 3 Aliphatic region of the ^{13}C -NMR spectrum of the PSt-*b*-PEB block copolymer.

EESEE, SEES, and SSES sequences, confirmed the block structure of the PSt-*b*-PEB block copolymers. The resonances from chain ends and the junctions between the two blocks (SSSEE sequence) could not be observed because of the lower sensitivity of ^{13}C -NMR. The peaks at δ values of 36.8 and 38.6 ppm, denoting an EEBBEE sequence, were not observed either, and this indicated that ethyl branches were distributed along the polyethylene segments in an isolated manner.

Figure 4 shows representative FTIR spectra of PSt-*b*-PBd and corresponding PSt-*b*-PEB block copolymers.

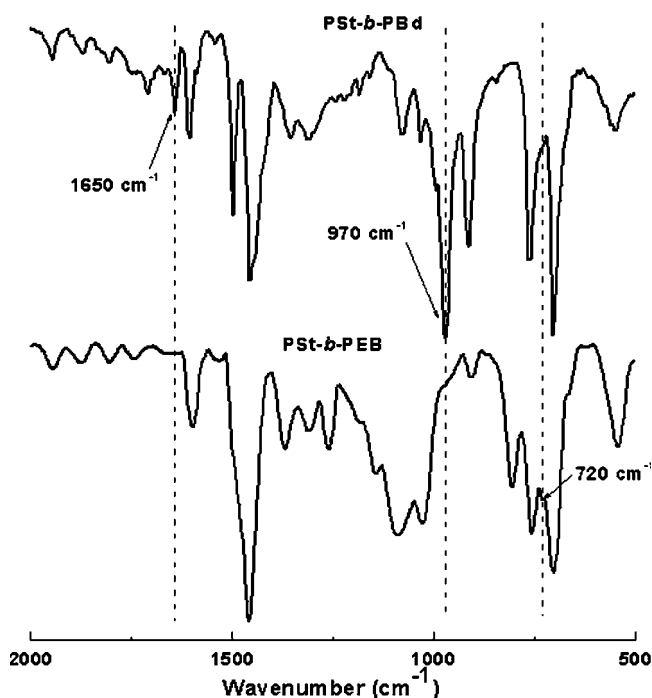


Figure 4 Representative FTIR spectra of PSt-*b*-PBd and corresponding PSt-*b*-PEB block copolymers.

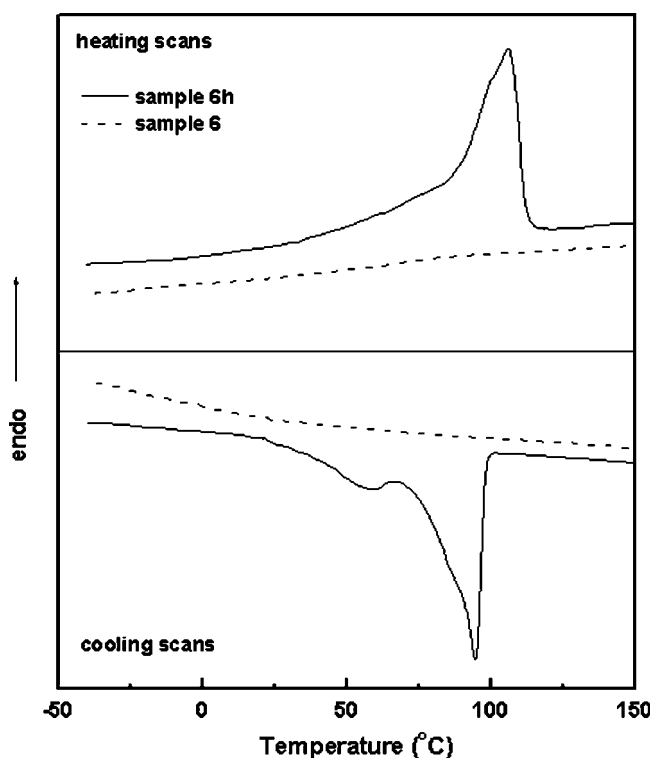


Figure 5 DSC curves of PSt-*b*-PBd and corresponding PSt-*b*-PEB block copolymers.

The absorbance band at 1650 cm^{-1} from double bonds and the band at 970 cm^{-1} produced by trans-1,4-addition in the polybutadiene block of PSt-*b*-PBd disappeared after selective hydrogenation, whereas a new absorbance band appeared at 720 cm^{-1} , overlapping the absorbance bands of PSt at 700 and 760 cm^{-1} , ascribed to the CH_2 rocking vibration in the PEB block.

Figure 5 shows the DSC curves of samples 6 and 6h in Table I. No pronounced exothermic and endothermic peaks can be observed in the cooling and heating scans of sample 6, respectively. In sharp contrast, a pronounced exothermic peak at $\sim 94^\circ\text{C}$ and a strong endothermic peak at $\sim 106^\circ\text{C}$ can be observed in the cooling and heating scans of sample 6h, respectively, which are close to the crystallization temperature and melting temperature of linear low-density polyethylene. The DSC curves for other PSt-*b*-PEB block copolymers were similar and are not presented here. This also shows that the formation of crystallizable PEB blocks via the hydrogenation of unsaturated PBd blocks.

CONCLUSIONS

A series of PSt-*b*-PBd block copolymers were synthesized by the sequential anionic polymerization of styrene and butadiene monomers. The PSt-*b*-PBd block copolymers were converted to the corresponding PSt-*b*-PEB block copolymers through selective hydrogenation of the unsaturated PBd block. GPC, ^1H -NMR, ^{13}C -

NMR, FTIR, and DSC analyses confirmed the formation of semicrystalline PSt-*b*-PEB block copolymers without changes in the chain lengths of the two blocks and molecular weight distribution. The results show that noncatalytic hydrogenation with diimide as the hydrogen source is a simple and quantitative method for the selective hydrogenation of PBd-containing polymers into saturated polymers.

References

1. Yu, J. M.; Dubois, P.; Jerome, R. *Macromolecules* 1996, 29, 8362.
2. Wang, S. M.; Chang, J. R.; Tsiang, R. C. C. *Polym Degrad Stab* 1996, 52, 51.
3. Rao, P. V. C.; Upadhyay, V. K.; Pillai, S. M. *Eur Polym J* 2001, 37, 1159.
4. Schipper, F. J. M.; Floudas, G.; Pispas, S.; Hadjichristidis, N.; Pakula, T. *Macromolecules* 2002, 35, 8860.
5. Schmalz, H.; Knoll, A.; Muller, A. J.; Abetz, V. *Macromolecules* 2002, 35, 10004.
6. Pispas, S.; Siakali-Kioulafa, E.; Hadjichristidis, N.; Mavromoustakos, T. *Makromol Chem Phys* 2002, 203, 1317.
7. Yu, J. M.; Yu, Y. S.; Dubois, P.; Teyssie, P.; Jerome, R. *Polymer* 1997, 38, 3091.
8. Imaizumi, K.; Ono, T.; Natori, I.; Sakurai, S.; Takeda, K. *J Polym Sci Part B: Polym Phys* 2001, 39, 13.
9. Gehlsen, M. D.; Bates, F. S. *Macromolecules* 1994, 27, 3611.
10. Ness, J. S.; Brodil, J. C.; Bates, F. S.; Hahn, S. F.; Hucul, D. A.; Hillmyer, M. A. *Macromolecules* 2002, 35, 602.
11. Zaera, F. *Langmuir* 1996, 12, 88.
12. Tsiang, R. C. C. *Polym Mater Sci Eng* 1999, 80, 481.
13. Tsiang, R. C. C.; Yang, W. S.; Tsai, M. D. *Polymer* 1999, 40, 6351.
14. Yang, W. S.; Hsieh, H. C. C.; Tsiang, R. C. C. *J Appl Polym Sci* 1999, 72, 1807.
15. Chiang, W. L.; Hsieh, H. C. C.; Tsiang, R. C. C. *J Polym Res Taiwan* 1998, 5, 227.
16. Harwood, H. J.; Russell, D. B.; Verthe, J. J. A.; Zymonas, J. *Makromol Chem* 1973, 163, 1.
17. Mango, L. A.; Lenz, R. W. *Makromol Chem* 1973, 163, 13.
18. Parker, D. K.; Roberts, R. F.; Schiessl, H. W. *Rubber Chem Technol* 1994, 67, 288.
19. Podesva, J.; Holler, P. *J Appl Polym Sci* 1999, 74, 3203.
20. Grassi, A.; Caprio, M.; Zambelli, A.; Bowen, D. E. *Macromolecules* 2000, 33, 8130.
21. Hahn, S. F. *J Polym Sci Part A: Polym Chem* 1992, 30, 397.
22. Xu, J. T.; Jin, W.; Fan, Z. Q. *J Appl Polym Sci* 2005, 98, 208.
23. Hsieh, H.; Quirk, R. P. *Anionic Polymerization: Principles and Practical Applications*; Marcel Dekker: New York, 1996.
24. Huang, D. C.; Lin, Y. C.; Tsiang, R. C. C. *J Polym Res Taiwan* 1995, 2, 91.
25. Huang, D. C.; Tsiang, R. C. C. *J Appl Polym Sci* 1996, 61, 333.
26. Lin, Y. C.; Tsiang, R. C. C. *J Appl Polym Sci* 1997, 64, 2543.
27. Sierra, C. A.; Galan, C.; Fatou, J. G.; Parellada, M. D.; Barrio, J. A. *Polymer* 1997, 38, 4325.
28. *Physical Properties of Polymers Handbook*; Mark, J. E., Ed.; AIP: New York, 1996.