

Synthesis and Characterization of Low-Molecular-Weight Hydrogenated Polybutadiene-*b*-Poly(ethylene glycol) Block Copolymers

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ABSTRACT: Low-molecular-weight hydrogenated polybutadiene-*b*-poly(ethylene glycol) (HPBd-*b*-PEG) block copolymers with double crystallizable blocks were synthesized by the coupling of hydroxyl-end-group-containing hydrogenated polybutadiene and poly(ethylene glycol) with terephthaloyl chloride as a coupling reagent. The block structure was confirmed by ¹H-NMR, and the molecular weights of the blocks were determined as well. Gel permeation chromatography showed that the HPBd-*b*-PEG block copolymers had narrow molecular weight distributions. The crystallization and superstructures of the HPBd-*b*-PEG block

copolymers were studied with differential scanning calorimetry, wide-angle X-ray diffraction (WAXD), and polarized optical microscopy. The results revealed that the crystallization of both blocks was suppressed mutually, especially for the shorter block. WAXD patterns showed that the crystal structures remained unchanged for both blocks. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 208–215, 2005

Key words: block copolymers; crystallization; polybutadiene; synthesis

INTRODUCTION

Recently, the crystallization of block copolymers has attracted many researchers. Because of the competition of microphase separation and crystallization on the nanoscale, semicrystalline block copolymers can exhibit a versatile morphology^{1–13} that depends on the crystallization conditions and characteristics of the block copolymers.^{14,15} As a result, crystallization is an effective way of regulating and controlling the morphology of block copolymers. So far, most reports have concentrated on block copolymers containing a single crystallizable block. By contrast, only a few block copolymers containing double crystallizable blocks have been studied, and most reports are limited to the poly(ϵ -caprolactone)-*b*-poly(ethylene oxide) diblock copolymer.^{16–30} In this study, another type of block copolymer containing double crystallizable blocks, hydrogenated polybutadiene-*b*-poly(ethylene glycol) (HPBd-*b*-PEG), was synthesized. HPBd-*b*-PEG was obtained by the hydrogenation of polybutadiene-*b*-poly(ethylene glycol) (PBd-*b*-PEG). There are usually two ways of synthesizing PBd-*b*-PEG with a nar-

row molecular weight distribution in the literature. In the first way, polybutadiene (PBd) with a hydroxyl end group is synthesized by living anionic polymerization, and then the hydroxyl end group is transformed into active species that can initiate the living anionic ring-open polymerization of ethylene oxide.^{31,32} In the second way, PBd-*b*-PEG is synthesized by the sequential living anionic polymerization of butadiene and ethylene oxide without the transformation of active species in the presence of a special base.^{33,34} In this work, HPBd-*b*-PEG was synthesized by the coupling of hydroxyl-end-group-containing hydrogenated polybutadiene (HPBd) and poly(ethylene glycol) (PEG), and the crystallization and morphology of HPBd-*b*-PEG were preliminarily studied.

EXPERIMENTAL

Synthesis of polybutadiene with —OH end groups (PBd-OH)

A cyclohexane solvent (50 mL) was injected into a flask equipped with a magnetic stirrer and connected to a Schlenk line. Butadiene gas was introduced and dissolved in cyclohexane, and then the mixture was weighed to determine the amount of butadiene dissolved. The concentration of butadiene was controlled between 10 and 15 g/100 mL. A prescribed amount of *n*-butyl lithium (*n*-BuLi), which was calculated in terms of the weight of butadiene and the targeted molecular weight of

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PBd, was injected into the flask. The polymerization reaction was carried out at 45°C for 7 h. Subsequently, the mixture in the flask was cooled below 10°C, and ethylene oxide was injected. A small amount of *n*-BuLi was added to ethylene oxide to consume any active impurity before injection. The amount of ethylene oxide was about 5 times greater than the normal amount needed to make sure that each polymer chain end reacted with ethylene oxide. The hydroxylation reaction of the polymer chain ends lasted for 12 h at 8°C; then, the unreacted ethylene oxide was removed, and excessive 7% HCl was added at 40°C to terminate the reaction. The product was washed with water several times and dried *in vacuo* at 60°C overnight.

Hydrogenation of PBd-OH

The hydrogenation of PBd-OH was carried out in a three-necked flask equipped with a reflux condenser and a mechanical stirrer under an argon atmosphere. PBd-OH was first dissolved in xylene at a concentration of 22 g/L, and the antioxidant Irganox 1010 (0.1% w/v) was added. *p*-Toluenesulfonylhydrazide (TSH) was introduced at 100°C. The mixture was further heated to reflux with rigorous stirring, and the refluxing lasted 7 h. After the reaction was stopped, the solvent xylene was removed *in vacuo*, and solid powders were obtained. Methanol was added, and the mixture was stirred for 2 h and then filtered. The resultant polymer was extracted with methanol in a Soxhlet extractor for 8 h. No bis(*p*-tolyl)disulfide, the decomposition product of TSH, was detected in hydrogenated PBd-OH (HPBd-OH).

Coupling of HPBd-OH and PEG

Low-molecular-weight HPBd-OH was dissolved in CHCl₃ at 60°C. The concentration was 10% (w/v). The hot solution of HPBd-OH in CHCl₃ was dropped slowly into a solution of terephthaloyl chloride in CHCl₃ under rigorous stirring. The molar ratio of terephthaloyl chloride to HPBd-OH was 5:1. After reaction at 60°C for 24 h, CHCl₃ was evaporated, and the solid was washed with diethyl ether five times to remove unreacted terephthaloyl chloride. The reaction product of HPBd-OH with terephthaloyl chloride was dissolved in CHCl₃ at 60°C again, and the concentration was 10% (w/v). The hot solution was dropped slowly into the solution of PEG in CHCl₃ under rigorous stirring. The temperature of the PEG solution was maintained at 60°C, and the concentration of PEG was 10% (w/v). The molar ratio of PEG to HPBd-OH was 5:1 to ensure that all HPBd-OH molecules were reacted. When all the solution of HPBd-OH was added, the mixture was refluxed for 24 h. The solvent CHCl₃ was evaporated, and a large amount of ethanol was

added to dissolve the unreacted PEG. The insoluble product was washed with ethanol three times and then was extracted with *n*-hexane with a Soxhlet extractor for 24 h to remove a small amount of unreacted HPBd-OH.

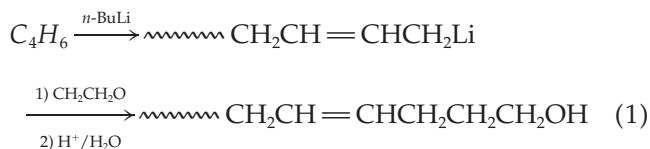
Characterization

The molecular weight distribution of PBd-OH and PEG was characterized with a Waters (Milford, MA) 150C gel permeation chromatography (GPC) instrument at 25°C with toluene as a solvent. Because HPBd was insoluble in toluene at room temperature, the molecular weight distribution of HPBd-*b*-PEG was characterized by GPC at 135°C with trichlorobenzene as a solvent. The number-average molecular weight (M_n) of PBd-OH and the molecular weight of the blocks in HPBd-*b*-PEG were determined with ¹H-NMR on a Bruker (Rheinstetten, Germany) Avance MX500 spectrometer. For PBd-OH, the NMR experiments were carried out at room temperature with chloroform-*d*₁ as a solvent, whereas for the block copolymers, high-temperature experiments (70°C) were conducted with *o*-chlorobenzene-*d*₄ as a solvent. Infrared (IR) spectroscopy was carried out on a Bruker (Ettlingen, Germany) Vector 22 spectrometer. The melting and crystallization behavior was determined on a PerkinElmer (Boston, MA) Pyris-1 differential scanning calorimetry (DSC) instrument. About 4–5 mg of the samples was heated to 200°C and held for 5 min to erase the thermal history, and then the samples were cooled to –50°C at a rate of 10°C/min and finally were heated to 160°C at a rate of 10°C/min. Wide-angle X-ray diffraction (WAXD) experiments were conducted on a Bruker (Cheshire, UK) D8 X-ray diffractometer (40 kV, 40 mA) with Ni-filtered Cu K α radiation (wavelength = 0.1542 nm) from 2 θ = 5° to 2 θ = 45° in increments of 0.02°. Polarized optical microscopy (POM) experiments were conducted on an Olympus (Tokyo, Japan) BX50 microscope connected to a digital camera. The samples for the POM experiments were first melted and then cooled to room temperature.

RESULTS AND DISCUSSION

Synthesis of PBd-OH

The living anionic polymerization of butadiene was initiated by *n*-BuLi and then terminated by the addition of ethylene oxide to introduce an end hydroxyl group:



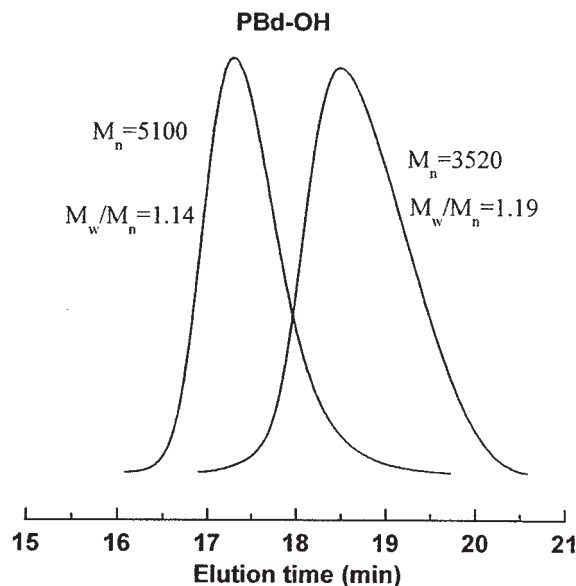


Figure 2 GPC curves of PBd-OH with different molecular weights.

Figure 1 shows the $^1\text{H-NMR}$ spectra of PBd and PBd-OH. A peak at $\delta = 3.7$ ppm appears in the spectrum of PBd-OH, but there is no such a peak in the spectrum of PBd. This shows that $-\text{OH}$ groups were successfully attached to the chain end of PBd. The assignment of the NMR peaks for PBd-OH is given in Figure 1(b), and M_n of PBd-OH can be calculated according to the following equation:

$$M_n = 14 \times \frac{(I_b + I_c + I_f)/2}{I_a/3} + 13 \times \frac{I_g + I_{g'} + I_h}{I_a/3} + 15 + 14 + 17 = 21 \times (I_b + I_c + I_f)/I_a + 39 \times (I_g + I_{g'} + I_h)/I_a + 46 \quad (2)$$

where I_a is the intensity of hydrogen atoms in the methyl end group originating from *n*-BuLi initiator, $I_b + I_c + I_f$ is the total intensity of hydrogen atoms in CH_2 (CH_2 connected to hydroxyl is not included) and $I_g + I_{g'} + I_h$ is the total intensity of hydrogen atoms in CH . The numbers 15, 14, and 17 are the molecular weights of the CH_3 end group, CH_2 connected to $-\text{OH}$, and the hydroxyl group, respectively. When the polymerization of butadiene was initiated by *n*-BuLi, 1,2-addition, which produced the NMR peaks *f* and *g'* in Figure 1(b), occurred as well as 1,4-addition. The molar percentage of 1,2-addition can be calculated:

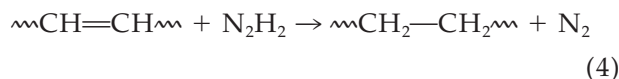
$$1,2\text{-Addition \%} = I_f/(I_g + I_f) \times 100\% \quad (3)$$

The molar percentages of 1,2-addition are 7.5 and 5.8 mol % for the PBd-OH samples with $M_n = 3520$ and $M_n = 5100$, respectively.

The GPC curves of two PBd-OH samples are shown in Figure 2. Both samples had a narrow molecular weight distribution [weight-average molecular weight/number-average molecular weight (M_w/M_n)].

Hydrogenation of PBd-OH

The pending vinyl groups and double bonds in the main chains of PBd-OH were hydrogenated with diazene on the basis of the following mechanism:^{35,36}



The unstable diazene was produced *in situ* by the thermolysis of TSH:

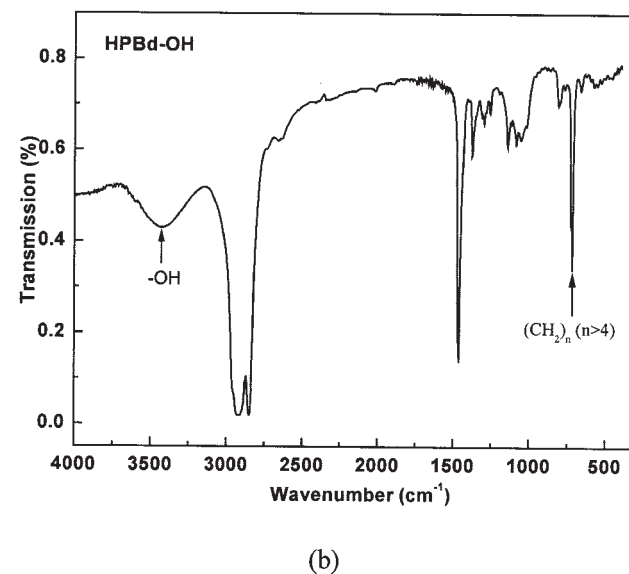
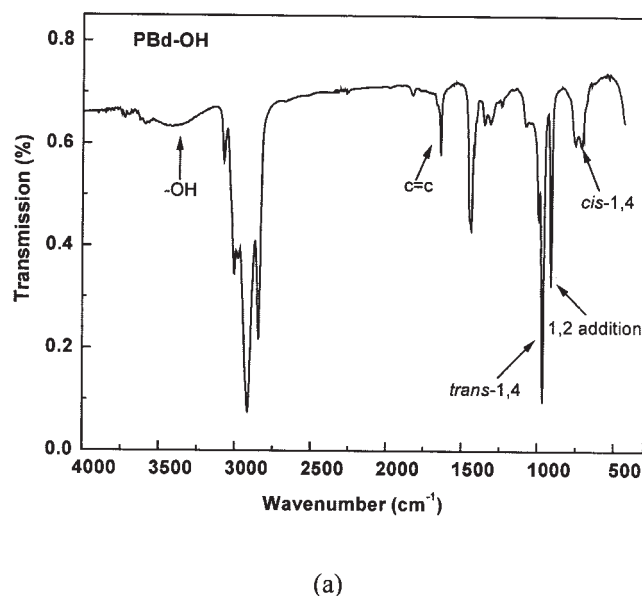


Figure 3 IR spectra of (a) PBd-OH and (b) HPBd-OH.

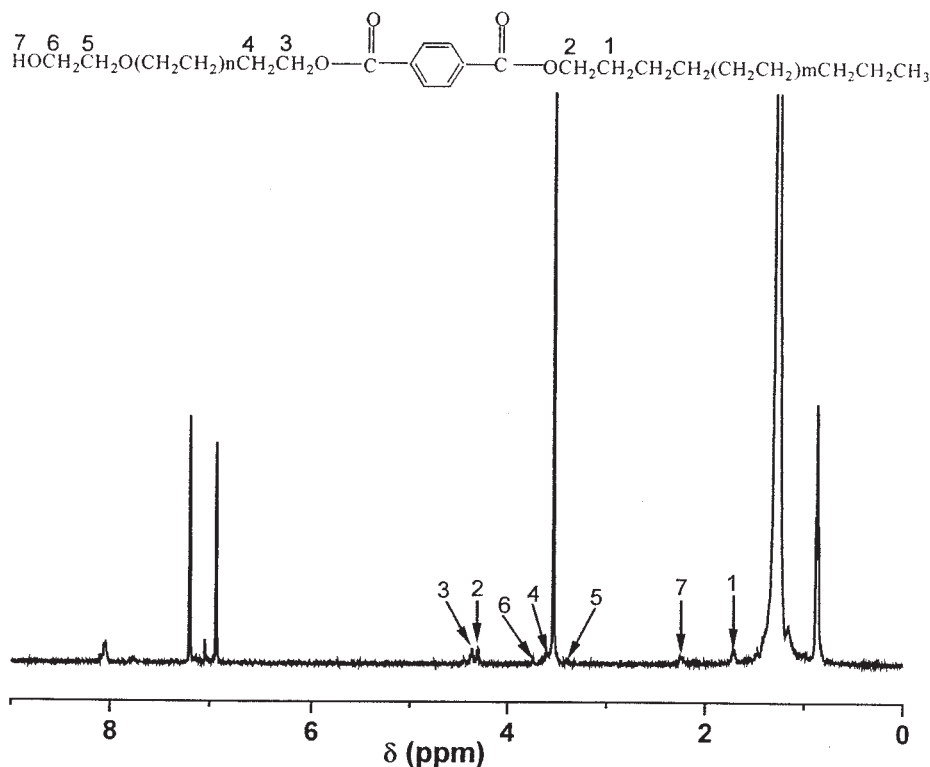
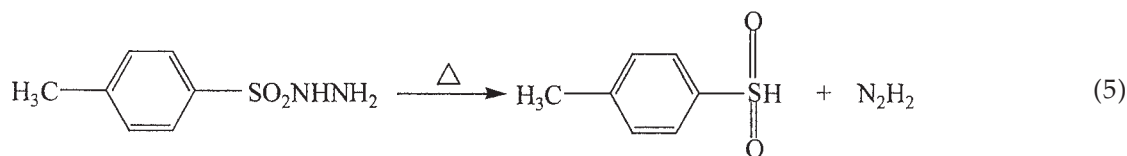


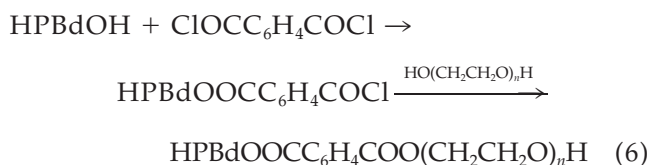
Figure 4 $^1\text{H-NMR}$ spectrum of HPBd-*b*-PEG.



Because the hydrogenation reaction proceeded at a high temperature, the hydrogenation reaction was conducted before the coupling reaction to avoid possible cleavage of the ester bonds. Figure 3 shows the IR spectra of PBd-OH and HPBd-OH. The bands at 1630, 967, 720–740, and 911 cm^{-1} , which were produced by a double bond, *trans*-1,4-addition, *cis*-1,4-addition, and 1,2-addition in PBd-OH, respectively, disappeared after hydrogenation, whereas the band for polyethylene, $(\text{CH}_2)_n$ ($n > 4$), appeared at 721 cm^{-1} in HPBd-OH. These show that the hydrogenation reaction was carried out successfully. After hydrogenation, the hydroxyl groups were retained.

Coupling of HPBd-OH and PEG

HPBd-*b*-PEG block copolymers were prepared by the coupling of HPBd-OH and PEG under suitable reaction conditions with terephthaloyl chloride as a coupling reagent:



The $^1\text{H-NMR}$ spectrum of one of the products is shown in Figure 4. At first glance, the peaks from double bonds in the range of $\delta = 5.0\text{--}6.0$ ppm cannot be observed, and this indicates that the block copolymer was saturated. This is in agreement with the IR results. Besides the $^1\text{H-NMR}$ signs from PEG and HPBd-OH, some weak resonances appear as well, which can be attributed to end groups and to the units near the coupling reagent. The assignment of these weak peaks is given in Figure 4. On the basis of the intensities of these weak peaks and the peak intensities of HPBd-OH and PEG, the M_n values of HPBd-OH and PEG in the block copolymers can be calculated:

$$M_n^{\text{PEG}} = \left(\frac{I_{\text{PEG}}}{2I_6} + 1 \right) \times 44 \quad (7)$$

TABLE I
 M_n and M_w/M_n of PBd-OH, PEG, and Two Blocks in the Block Copolymers

Sample	PBd-OH		PEG		HPBd- <i>b</i> -PEG			
	M_n	M_w/M_n	M_n	M_w/M_n	M_n^{HPBd}	M_n^{PEG}	W_{PEG}	M_w/M_n
A	3520	1.14	500	1.14	3710	410	0.099	1.31
B	3520	1.14	600	1.15	3600	620	0.147	1.25
C	5100	1.19	1500	1.15	4870	1570	0.244	1.22
D	5100	1.19	2500	1.16	4930	2340	0.322	1.27

W_{PEG} is the weight percentage of PEG in the block copolymers.

$$M_n^{\text{HPBdOH}} = \left(\frac{I_{\text{HPBdOH}}}{I_2} + 1 \right) \times 14 \quad (8)$$

The molecular weights for the starting materials HPBd-OH and PEG and for the block copolymers synthesized are listed in Table I. After purification, the molecular weights of HPBd-OH and PEG in the block copolymers were slightly different from those in the starting materials. The GPC elution curves of the block copolymers are illustrated in Figure 5. All four block copolymers basically had narrow molecular weight distributions. However, there still is a weak shoulder peak corresponding to the low molecular weight in sample A, which may have resulted from a small amount of unreacted HPBd-OH.

Crystallization and melting behaviors

The nonisothermal crystallization and subsequent melting DSC traces of the HPBd-*b*-PEG block copolymers are illustrated in Figures 6 and 7, respectively. In all the samples, the HPBd blocks showed a broad crystallization temperature range. The crystallization temperatures of the HPBd block in samples A and B

were different from those in samples C and D to some extent because of the different molecular weights and ethyl branches. On the other hand, the crystallization behavior of the PEG blocks was remarkably different for the various samples. The PEG block exhibited no crystallization peak in sample A, and this indicated that the crystallization of the PEG block was totally suppressed. In samples B and C, although the PEG blocks were crystallizable, the crystallization temperatures were quite low, falling into the typical temperature range of homogeneous nucleation. In contrast, the PEG block in sample D had a normal crystallization temperature. One can see from Figure 7 that the HPBd blocks in samples C and D, which had higher crystallization temperatures, also exhibited higher melting temperatures. There was no melting peak for the PEG block in sample A, in accordance with the disappearance of its crystallization peak. The PEG

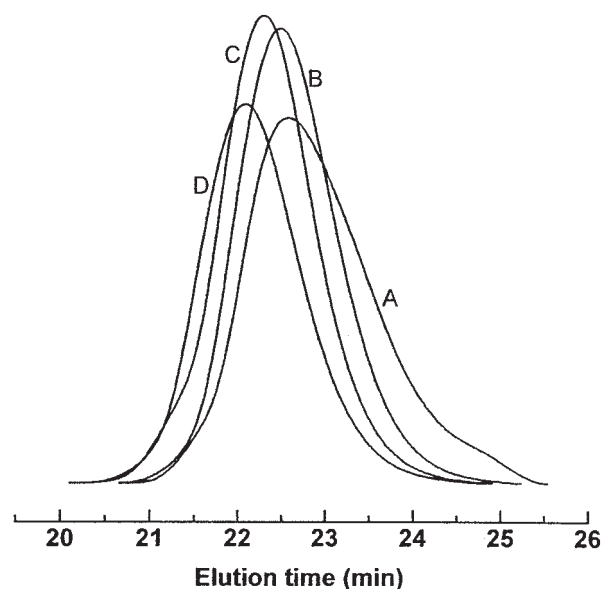


Figure 5 GPC curves of HPBd-*b*-PEG block copolymers.

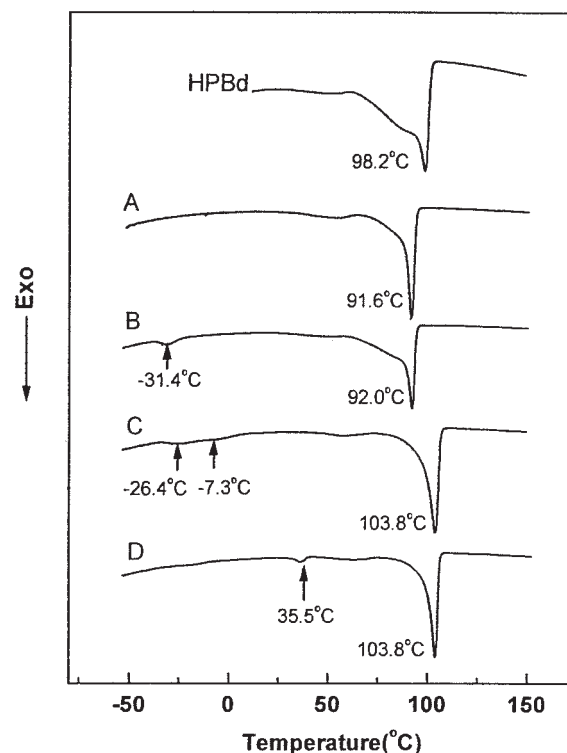


Figure 6 Nonisothermal crystallization DSC traces of HPBd and HPBd-*b*-PEG block copolymers.

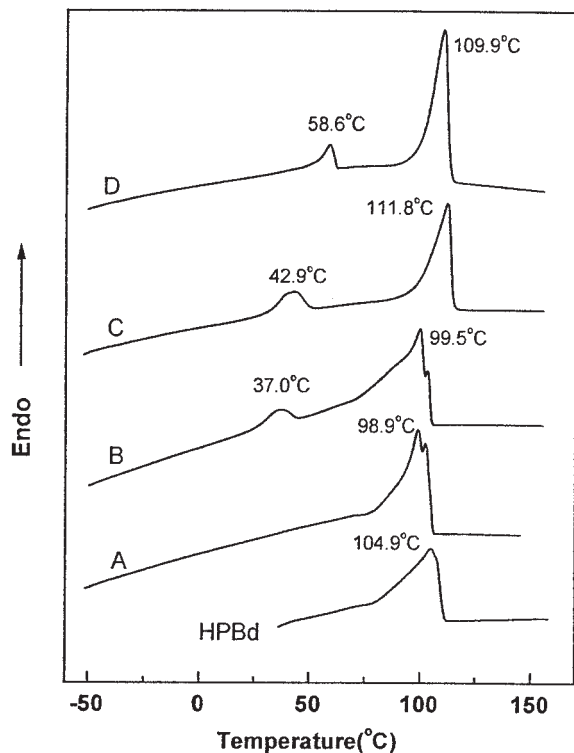


Figure 7 DSC melting traces of HPBd and HPBd-*b*-PEG block copolymers.

blocks in the other three samples exhibited normal melting temperatures. The larger difference in the melting temperature and crystallization temperature for samples B and C shows that larger supercooling was required for the crystallization of the PEG block in these two samples. DSC results reveal that in samples B and C the pre-existing polyethylene crystals may have provided a confined environment for the crystallization of PEG, leading to homogeneous nucleation and lower melting temperatures of PEG blocks. In contrast, crystallization of the PEG block in sample D was not confined, and the nucleation mechanism was heterogeneous; thus, sample D had normal crystallization and melting temperatures.

WAXD

Figure 8 shows the WAXD patterns of the HPBd-*b*-PEG block copolymers and HPBd. All four block copolymers exhibited typical WAXD patterns of polyethylene with an orthorhombic crystal structure: the (110) reflection at $2\theta = 21.6^\circ$, the (200) reflection at $2\theta = 24.0^\circ$, and a diffused peak attributed to amorphous polyethylene at $2\theta = 19.6^\circ$. However, with an increase in the PEG content in the block copolymers, the WAXD peaks contributed by PEG also became more evident. The WAXD peaks of PEG appear at $2\theta = 19.4^\circ$ for the (120) reflection and at $2\theta = 23.9^\circ$ for the (032

+ 112) reflection, which correspond to a monoclinic crystal structure of PEG. Although the WAXD peaks of PEG overlap with the diffused amorphous peak and (200) reflection peak of HPBd, one still can see from Figure 8 that for the block copolymer with a higher PEG content, the peak at $2\theta = 19.4^\circ$ became sharper and the shoulder peak at $2\theta = 23.9^\circ$ became more obvious. By contrast, block copolymers A and B, which had lower PEG contents, showed WAXD patterns similar to that of HPBd, and this indicated that the crystallization of PEG in these two block copolymers was severely suppressed.

Superstructure

The POM graphs of HPBd, PEG, and the HPBd-*b*-PEG block copolymers are shown in Figure 9. HPBd exhibited axialite crystals, whereas PEG showed a spherulite morphology. The morphology of the HPBd-*b*-PEG block copolymers was more like that of HPBd instead of PEG, and no spherulites were observed. This is not contrary to our expectation and agrees with the results of DSC and WAXD because HPBd was the major component in these four block copolymers. As the content of PEG increased, the crystalline particles became smaller, and the morphology became more homogeneous. This shows that PEG had an unfavorable effect on the crystallization of HPBd as well, and it was difficult for the HPBd block to form a superstructure at higher PEG contents. In combination with DSC, WAXD, and POM results, one can see that the crystallization of both blocks in the HPBd-*b*-PEG block copolymers was mutually affected, but the major component had a stronger suppression effect on the crystallization of the minor component.

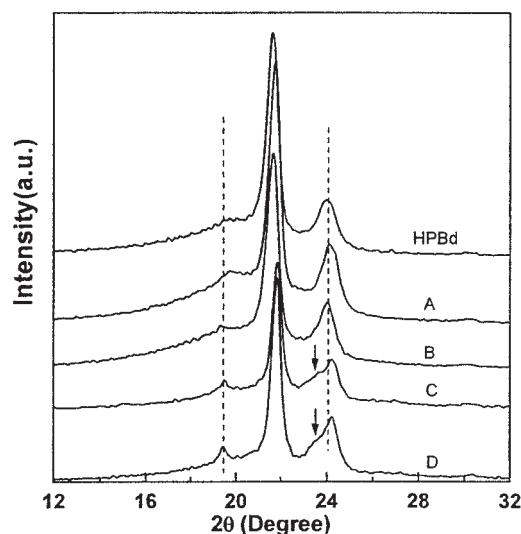


Figure 8 WAXD patterns of HPBd and HPBd-*b*-PEG block copolymers.

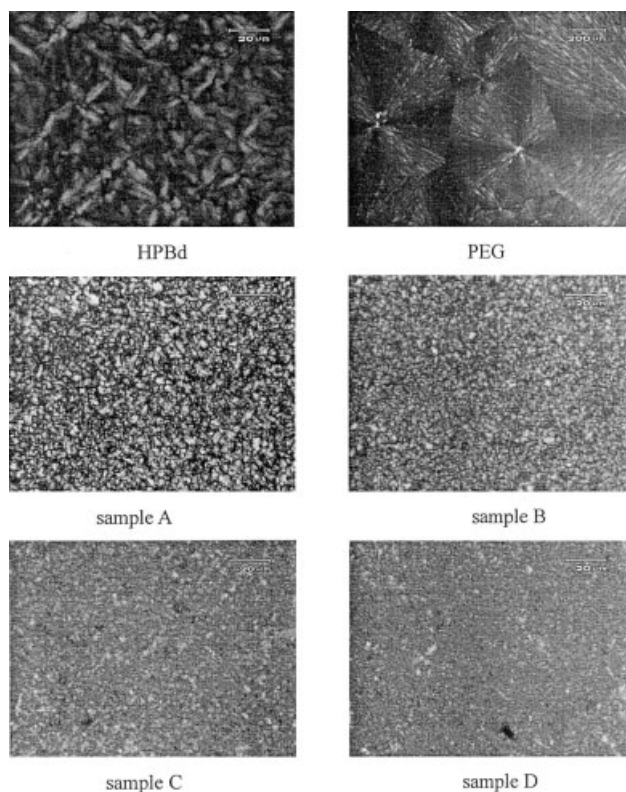


Figure 9 POM graphs of HPBd, PEG, and the HPBd-*b*-PEG block copolymers.

CONCLUSIONS

The formation of the block structure was verified by $^1\text{H-NMR}$, and the M_n values of the blocks were determined as well. GPC showed that all the block copolymers had narrow molecular weight distributions. The melting and crystallization behaviors showed that in the block copolymers with low contents of PEG block, crystallization of the PEG block may have been totally suppressed or was initiated by a homogeneous nucleation mechanism. At high contents, the PEG block crystallized via a heterogeneous nucleation mechanism. The POM graphs revealed that the PEG block also interfered with crystallization of the HPBd block. The crystal structures of the HPBd and PEG blocks in the block copolymers were similar to that of the corresponding homopolymer.

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