Synthesis of New Amphiphilic Diblock Copolymers Containing Poly(ethylene oxide) and Poly(α-olefin)

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ABSTRACT: This article discusses an effective route to prepare amphiphilic diblock copolymers containing a poly(ethylene oxide) block and a polyolefin block that includes semicrystalline thermoplastics, such as polyethylene and syndiotactic polystyrene (s-PS), and elastomers, such as poly(ethylene-*co*-1-octene) and poly(ethylene-*co*-styrene) random copolymers. The broad choice of polyolefin blocks provides the amphiphilic copolymers with a wide range of thermal properties from high melting temperature ~270 °C to low glass-transition temperature ~−60 °C. The chemistry involves two reaction steps, including the preparation of a borane group-terminated polyolefin by the combination of a metallocene catalyst and a borane chain-transfer agent as well as the interconversion of a borane terminal group to an anionic ($—O^-K^+$) terminal group for the subsequent ring-opening polymerization of ethylene oxide. The overall reaction process resembles a transformation from the metallocene polymerization of α-olefins to the ring-opening polymerization of ethylene oxide. The well-defined reaction mechanisms in both steps provide the diblock copolymer with controlled molecular structure in terms of composition, molecular weight, moderate molecular weight distribution ($M_w/M_n < 2.5$), and absence of homopolymer. © 2002 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 40: 3416–3425, 2002

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INTRODUCTION

Recently, we reported a convenient synthesis route[1] for preparing borane group-terminated polyolefins that is applicable to a broad range of polyolefin polymers from thermoplastics,[2] including polyethylene (PE), polypropylene (PP), and syndiotactic polystyrene (*s*-PS), to elastomers,[3] such as poly(ethylene-*co*-propylene) and poly(ethylene-*co*-1-octene). The chemistry was based on a B–H chain-transfer reaction during metallocene-mediated olefin polymerization. The terminal borane group was quantitatively converted to various functional groups, such as the OH group, and was selectively oxidized to form a stable polymeric radical for living free-radical polymerization[4,5] of functional monomers to prepare diblock copolymers, such as PE-*b*-PMMA and s-PS-*b*-PMMA. This process resembles a transformation reaction from metallocene polymerization to living free-radical polymerization via a borane terminal group to produce functional polyolefin diblock copolymers containing a polyolefin block and a free-radical-prepared functional (polar) polymer with well-controlled molecular structure.

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It is very interesting to expand this synthesis strategy to another route such as the transformation from metallocene to living ring-opening polymerization of cyclic ether, esters, amides, and so forth that would afford another set of diblock copolymers containing a polyolefin block and a condensation polymer block.

Amphiphilic copolymers,[6] containing hydrophobic and hydrophilic blocks, have attracted a great deal attention because of their interesting surface properties. They are ideal candidates for many applications[7–9] such as emulsifiers, dispersants, stabilizers, and antiforming agents in aqueous solution as well as surface modifiers for plastics and compatibilizers in polymer blends and composites. Among them, the most extensively examined and industrially significant ones are the amphiphilic copolymers containing a nonionic poly(ethylene oxide) (PEO)[10] as the hydrophilic block, which is water soluble, safe, and biocompatible, and a hydrophobic block on the basis of PPO,[11–13] polystyrene,[14–18] and polydienes.[19–22] An essential requirement for many applications is the precise control of the copolymer structure in terms of composition, molecular weight, molecular weight distribution, and the balance between hydrophobicity and hydrophilicity.

Two preferred synthesis routes in the synthesis of PEO-based amphiphilic block copolymers include sequential ring-opening polymerization,[23,24] used in the preparation of PEO/PPO and PEO/PCL copolymers, and chain extension involving ethylene oxide from a well-defined chain end-functionalized polymer[25–28] (including polystyrene, polybutadiene, polyisoprene, etc.) that is usually prepared by living (anionic, cationic, or free radical) polymerization. To further broaden the amphiphilic block copolymer to include polyolefin segment, several reports showed hydrogenation of the anionic prepared polyisoprene and polybutadiene to ethylene-*co*-propylene[29] and ethylethylene,[30] respectively. By means of extra reaction steps, some isomers (via 1,2-, 3,4-, or 1,4-addition) are present in the anionic-prepared polyisoprene and polybutadiene polymers that result in the hydrogenated polymer being slightly different from the corresponding polyolefin prepared by traditional transition-metal (Ziegler–Natta and metallocene) polymerization. On the basis of our knowledge, there is no amphiphilic diblock copolymer having PEO and poly(α-olefin) that is directly prepared from a transition-metal coordination polymerization mechanism, especially the ones prepared by metallocene catalysis with narrow molecular weight and compositional distributions. It would be very interesting to have an amphiphilic diblock copolymer containing PE and PEO blocks that is composed of two simple monomers with opposite philicity. In solid state, both polymer blocks should show extreme incompatibility, and they might be crystallized into two distinctive hydrophobic/hydrophilic crystalline phases with various morphological patterns controlled by the mole ratio of the two polymer blocks.

EXPERIMENTAL

Instrumentation and Materials

All ^{1}H NMR spectra were recorded on a Bruker AM 300 instrument with deuterated solvent (1,1,2,2-tetrachloroethane-*d*) and tetramethylsilane as an internal standard. The molecular weight and distribution of the polymers were determined by gel permeation chromatography (GPC) with a Waters GPC 600E with a Waters 410 Differential Refractometer. The columns used were Waters Ultrastyragel of 10^5, 10^4, 10^3 and 500 Å. A flow rate of 1.0 mL/min was used, and the mobile phase was tetrahydrofuran (THF) at 35 °C. Narrow molecular weight PS samples were used as standards for calibration. Differential scanning calorimetry (DSC) was performed on a PerkinElmer 7 Series thermal analysis system at the second scanning with the rate of 20 °C/min. Scanning electron microscopy (SEM) was used to view some of the polymer films with a Topcon International Scientific Instruments ISI-SX-40 using secondary electron imaging. SEM samples were prepared from films cryo-fractured in liquid N_2. Samples were mounted on an aluminum stub and carbon coated to form a conductive coating.

All O_2 and moisture-sensitive manipulations were carried out inside an argon-filled drybox. Toluene and THF were dried by stirring with sodium naphthalide under argon and distilled out before use. Ethylene oxide (Aldrich) was distilled over CaH_2 after mixing at 0 °C for 5 h. $B(C_6F_5)_3$ (Aldrich) was sublimated before use. High-purity-grade ethylene (MG Industries), methanol, and 9-BBN (Aldrich) were purchased and used as received. The metallocene catalysts, including $[Cp^*{}_2ZrMe]^+[MeB(C_6F_5)_3]^-$, $[C_5Me_4(SiMe_2N^tBu)TiMe]^+[MeB(C_6F_5)_3]^-$, and $[Cp^*TiMe_2]^+[MeB(C_6F_5)_3]^-$ were prepared according to the published procedures.[31–33] Potassium naphthalide was prepared in THF by mixing

Table 1. Summary of PE-*b*-PEO Diblock Copolymers

	Reaction Conditions[a]							T_m[d] (°C)		ΔH_f[d] (J/g)	
Entry	M_n of PE ($\times 10^{-3}$ g/mol)	EO (mL)	Time (h)	Yield (g)	EO Conversion (%)	EO Content in Copolymers[b] (mol %)	M_n of Copolymers[c] ($\times 10^{-3}$ g/mol)	PEO	PE	PEO	PE
A1	10	1.5	48	3.0	75.2	40	20.1	21	109	11.85	109.3
A2	10	2.5	48	3.9	85.8	45	22.4	25	106	8.096	115.2
A3	10	4.0	48	5.1	87.5	62	34.9	55	102	14.78	106.4
A4	10	5.0	48	6.2	94.8	80	71.4	60	101	24.56	82.48
A5	19	4.0	48	5.14	88.9	50	76.0	60	133	49.96	96.61
A6	27	4.0	48	4.10	59.2	40	55.5	60	135	41.08	91.78

[a] Runs A1–A6 started with 2 g of PE-*t*-OK; solvent: 30 mL of THF; temperature = 80 °C.
[b] Determined by ^{1}H NMR.
[c] Estimated from ^{1}H NMR results.
[d] Determined by DSC, the second scanning rate 20 °C/min.

an excess of freshly cut potassium under argon and stirring for 12 h.

Chain-Transfer Reaction in Metallocene-Mediated Olefin Polymerization

The borane-terminated polyethylene (PE-*t*-B) and syndiotactic polystyrene (*s*-PS-*t*-B) were prepared by $[Cp^*_2ZrMe]^+[MeB(C_6F_5)_3]^-$ and $[Cp^*TiMe_2]^+[MeB(C_6F_5)_3]^-$, respectively. In contrast, the borane-terminated poly(ethylene-*co*-styrene) [P(E-*co*-S)-*t*-B] and poly(ethylene-*co*-1-octene) [P(E-*co*-O)-*t*-B] were prepared by $[C_5Me_4(SiMe_2N^tBu)TiMe]^+[MeB(C_6F_5)_3]^-$. The detail experimental procedures have been discussed.[1–3]

Oxidation and Metallation of the Borane-Terminated Polyolefins

The oxidation of the borane terminal group is very effective in both homogeneous P(E-*co*-S)-*t*-B and P(E-*co*-O)-*t*-B and heterogeneous PE-*t*-B and *s*-PS-*t*-B reaction conditions. In a typical example, 2.0 g of PE-*t*-B [number-average molecular weight (M_n) = 2.5×10^4 g/mol; molecular weight distribution (M_w/M_n) = 2.2] were placed in a suspension of 50 mL of dry, O_2-free THF in a drybox. The sealed reactor was moved out and purged with nitrogen. To the polymer slurry, a solution containing 0.4 g of NaOH in 2 mL of H_2O and 0.5 mL of methanol (MeOH) purged by N_2 was added

Table 2. Summary of P(E-*co*-O)-*b*-PEO and P(E-*co*-S)-*b*-PEO Diblock Copolymers

	Reaction Conditions[a]			Diblock Copolymer			
Entry	M_n[b] ($\times 10^{-3}$ g/mol)	EO (mL)	Yield (g)	Conversion of EO (%)	EO Content[c] (mol %)	M_n[b] ($\times 10^{-3}$ g/mol)	M_w/M_n[b]
B1	121	1.0	2.64	72.2	25.0	150	2.4
B2	121	1.5	3.09	82.0	45.4	193	2.3
B3	121	2.0	3.65	93.1	53.5	221	2.4
B4	121	4.5	5.61	90.5	70.6	327	2.3
B5	121	6.5	7.28	91.7	78.7	441	2.3
C1	8	1.0	2.66	74.5	28.7	11	2.5
C2	20	1.0	2.84	94.8	33.9	28	2.4
C3	30	1.0	2.63	71.1	22.6	40	2.4
C4	42	1.5	2.97	73.0	31.1	63	2.3
C5	42	3.5	4.99	96.4	58.2	106	2.3

[a] Runs B1–B5 started with 2 g of P(E-*co*-O)-*t*-OK, containing ~40 mol % 1-octene in the copolymer; runs C1–C5 started with 2 g of P(E-*co*-S)-*t*-OK, containing ~30 mol % styrene in the copolymer; reaction temperature = 80 °C; reaction time = 48 h; and solvent: 30mL of THF.
[b] By GPC in THF using PS standards.
[c] By ^{1}H NMR.

at room temperature; then 1.6 mL of 30% oxygen-free H_2O_2 was added dropwise at 0 °C. The oxidation was performed at 40 °C for 6 h before being poured into 100 mL of MeOH. The resulting PE-*t*-OH solid was filtered and dried in a vacuum oven at 50 °C for 8 h.

The subsequent metallation reactions were carried out by using two reagents, dependent on the reaction conditions. Potassium naphthalide/THF solution was used in the heterogeneous cases involving PE-*t*-OH and *s*-PS-*t*-OH polymers. On the other hand, the fresh-cut potassium was directly used in the homogeneous cases involving P(E-*co*-S)-*t*-OH and P(E-*co*-O)-*t*-OH polymers. In a typical example, about 2 g of PE-*t*-OH (or *s*-PS-*t*-OH) were suspended in 30 mL of THF under nitrogen in a 150-mL flask. The solution was then stirred at 50 °C for 12 h before syringing in 2 mL (1 M) of potassium naphthalide/THF solution. After stirring the solution at 50 °C for 6 h, the polymer powder was filtered under argon gas and washed with dry THF several times. The resulting metallated polymer PE-*t*-OK (or *s*-PS-*t*-OK) was directly used in the subsequent ring-opening polymerization.

Anionic Ring-Opening Polymerization of Ethylene Oxide

The ring-opening polymerization was carried out in both homogeneous [P(E-*co*-S)-*t*-OK and P(E-*co*-O)-*t*-OK] and heterogeneous (PE-*t*-OK and *s*-PS-*t*-OK) reaction conditions in THF. In the drybox, the metallated polymer (2 g) was mixed with 30 mL of dry THF in a 150-mL autoclave reactor that was sealed and taken out of the drybox and then attached to a vacuum line. The desired quantity of ethylene oxide (shown in Tables 1 and 2) was transferred directly from ethylene oxide/CaH_2 mixed solution into the reactor. The anionic ring-opening polymerization of ethylene oxide was carried out at 80 °C for 48 h before termination by adding 10 mL of acidified MeOH and then 100 mL of diethyl ether. The precipitated polymer was washed with diethyl ether and dried under vacuum at 60 °C for 48 h. The copolymer was then extracted with boiling acetone to remove the PEO homopolymer, and in each case the amount of PEO was negligible.

RESULTS AND DISCUSSION

In this article, we discuss a new synthesis route to preparing a range of amphiphilic diblock copolymers containing a PEO block and a polyolefin block.

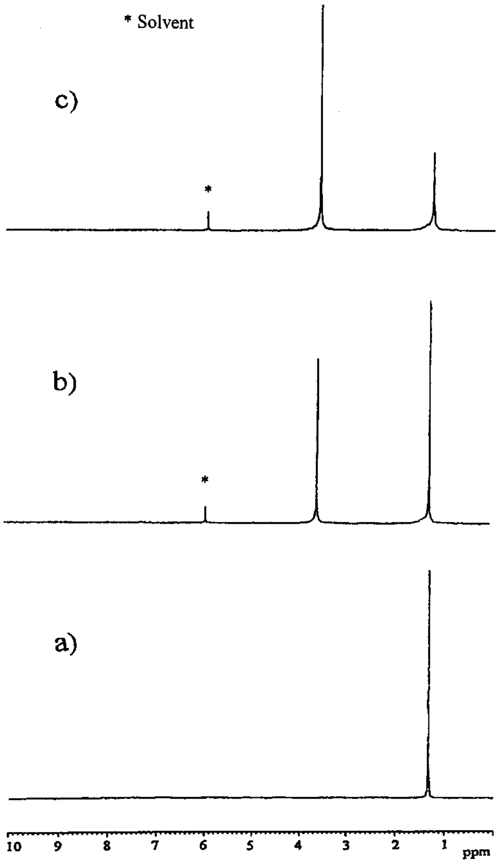
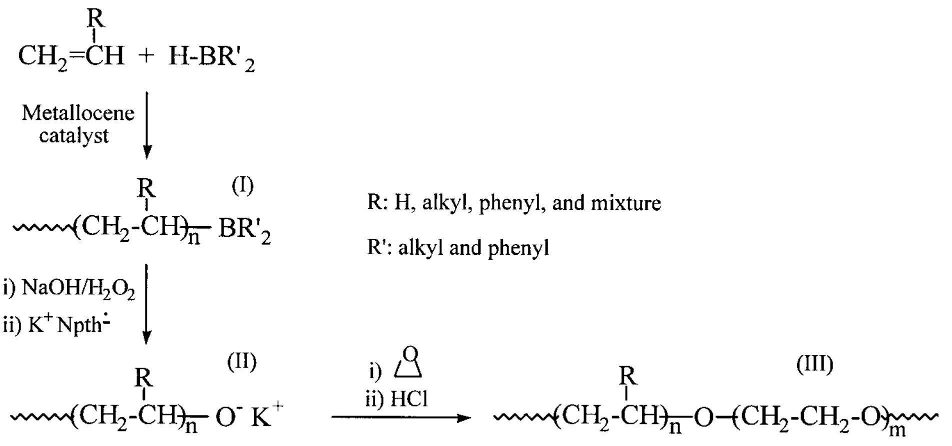


Figure 1. ^{1}H NMR spectra of (a) the starting PE-*t*-OH (M_n = 10 × 10^3 g/mol; M_w/M_n = 2.2) and two PE-*b*-PEO diblock copolymers (b) A-1 and (c) A-4 (solvent: 1,1,2,2-tetrachloroethane-*d*).

Equation 1 illustrates the polymerization scheme that is centered on the transformation of metallocene polymerization of α-olefin to anionic ring-opening polymerization of ethylene oxide via a reactive terminal group. In the presence of a dialkylborane (H-BR_2), the metallocene-mediated propagating polyolefin chain engages in a facile ligand-exchange reaction with a B–H group to form a borane-terminated polyolefin (I) with a narrow composition distribution. The molecular weight of the borane-terminated polyolefin is inversely proportional to the molar ratio of [borane]/[α-olefin]. The terminal borane group is then transformed to a suitable anionic initiator for ethylene oxide polymerization by oxidation of borane to a hydroxy group using NaOH/H_2O_2 reagent and subsequent metallation of the terminal OH group with potassium naphthalide to achieve a reactive potassium alkoxide group at the polyolefin chain end (II). The new end group is active for living anionic ring-opening polymerization of ethylene oxide to form the resulting diblock copolymer (III).



(1)

Crystalline–Crystalline Diblock Copolymer Systems

Table 1 summarizes the experimental results of several PE-*b*-PEO diblock copolymers containing crystalline–crystalline PE and PEO segments. They were prepared by three borane-terminated polyethylene (PE-*t*-B) polymers ($M_{\mathrm{n}} = 10 \times 10^3$, 19×10^3, and 27×10^3 g/mol; $M_{\mathrm{w}}/M_{\mathrm{n}} < 2.5$) obtained from $[(\mathrm{Cp}^*)_2\mathrm{ZrMe}]^+[\mathrm{B}(\mathrm{C}_6\mathrm{F}_5)_4]^-$ mediated ethylene polymerization using 9-BBN chain-transfer agent.

Figure 1 illustrates the ^{1}H NMR spectra of two PE-*b*-PEO copolymers (runs A-1 and A-4) prepared by the same starting PE-*t*-B polymer with different quantities of ethylene oxide. Compared with the starting PE-*t*-B [Fig. 1(a)], showing a major peak at 1.30 ppm for ($\mathrm{C}\mathbf{H}_2$—$\mathrm{C}\mathbf{H}_2$) units, a new peak at 3.53 ppm corresponding to the methoxy group ($\mathrm{C}\mathbf{H}_2\mathrm{O}$) in PEO increases its intensity with the increasing quantity of ethylene oxide. The intensity ratio of between 1.30 and 3.53 ppm was used to determine the mole ratio of [ethylene]/[ethylene oxide] in the diblock copolymer. The extensive solvent extraction of the resulting diblock copolymer yields no PEO homopolymer. Apparently, the PEO segment continuously grows with the supply of ethylene oxide, and a high-molecular-weight PE-*b*-PEO diblock copolymer with up to 80 mol % of PEO content [Fig. 1(c)] is obtained. In this reaction, using a relatively low-molecular-weight PE-*t*-B ($M_{\mathrm{n}} = 10 \times 10^3$ g/mol), the heterogeneous reaction condition seems to suggest no effect in the transformation and subsequent ring-opening polymerization. However, as the PE-*t*-B molecular weight increases to $M_{\mathrm{n}} > 27 \times 10^3$ g/mol, the chain-extension reaction becomes more difficult. Although no homopolymer of PEO was observed, the transformation reaction and anionic ring-opening polymerization are limited by the availability of end groups.

Figure 2 depicts the DSC curves of several PE-*b*-PEO copolymers (runs A-1, A-4, and A-6) that were prepared from two PE-*t*-B polymers (with $M_{\mathrm{n}} = 10 \times 10^3$ and 27×10^3 g/mol). The detailed results of the diblock copolymers are summarized in Table 1. Two distinctive melting endotherms are observed for each diblock copolymer indicating a clear phase separation between the hydrophobic and hydrophilic domains, and both the melting point (T_{m}) and the heat of fusion (ΔH_{f}) are affected by their molecular weight. Comparing runs A-1 and A-4, which have the same PE block, both the T_{m} and ΔH_{f} of the PEO block increase as its molecular weight increases. The T_{m} usually becomes constant (at ca. 60 °C) when the PEO molecular weight exceeds 30×10^3 g/mol. The T_{m} peak of the PE block in run A-4 is quite broad with reduced ΔH_{f}, signaling difficulty in the crystallization of the PE segment (with relatively low molecular weight), as it is surrounded by the high-molecular-weight PEO segment. The T_{m} of the PE block also increases with its molecular weight, reaching 135 °C (similar to that of HDPE) in run A-6, where the PE molecular weight excess 27×10^3 g/mol.

In general, similar results were also observed in other crystalline–crystalline amphiphilic diblock copolymers. Figure 3 compares the ^{1}H NMR spectra of a *s*-PS-*b*-PEO copolymer and the starting *s*-PS-*t*-B ($M_{\mathrm{n}} = 50 \times 10^3$ g/mol). Two aliphatic proton peaks at 1.32 and 1.85 ppm and two sharp aromatic proton peaks at 6.68 and 7.15 ppm are the signature of the highly syndiotactic arrangement of the styrene units in the polymers. The high syndiotacticity of the *s*-PS block was

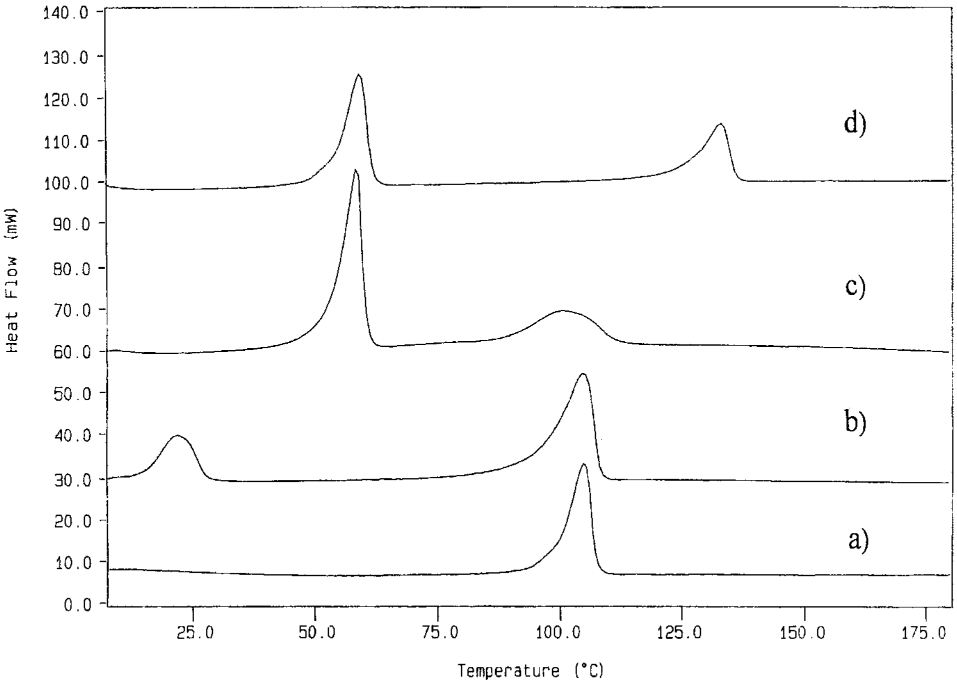


Figure 2. DSC curves of (a) the starting PE-*t*-OH ($M_n = 10 \times 10^3$ g/mol; $M_w/M_n = 2.2$) and three PE-*b*-PEO diblock copolymers (b) A-1, (c) A-4, and (d) A-6 (second heating cycle with the heating rate 20 °C/min).

also observed in the DSC curve with a high T_m endotherm (at ~270 °C). In Figure 3(b) a new chemical shift was observed at 3.53 ppm corresponding to the methoxy group (C**H**$_2$O) in PEO. The peak intensity ratio of between 1.32 and 3.53 ppm was used to determine the mole ratio of [styrene]/[ethylene oxide] in the diblock copolymer. Apparently, the chain extension with ethylene oxide in this system was not very efficient—only ~25 mol % ethylene oxide content in this high-molecular-weight *s*-PS-*b*-PEO copolymer.

Amorphous-Crystalline Diblock Systems

It is very interesting to investigate homogeneous reaction conditions with amorphous polyolefins, such as poly(ethylene-*co*-styrene) [P(E-*co*-S)] and poly(ethylene-*co*-1-octene) [P(E-*co*-O)]. The chain-extension process of forming diblock copolymer can be conveniently monitored by low-temperature GPC measurement. Figure 4 compares the GPC curves of three P(E-*co*-O)-*b*-PEO diblock copolymers, sampled during the chain-extension reaction of ethylene oxide, which are also compared to the starting borane-terminated P(E-*co*-O) polymer (M_n = 121,000 g/mol and M_w/M_nm = 2.2).

The polymer continuously increased its molecular weight during the entire polymerization pro-

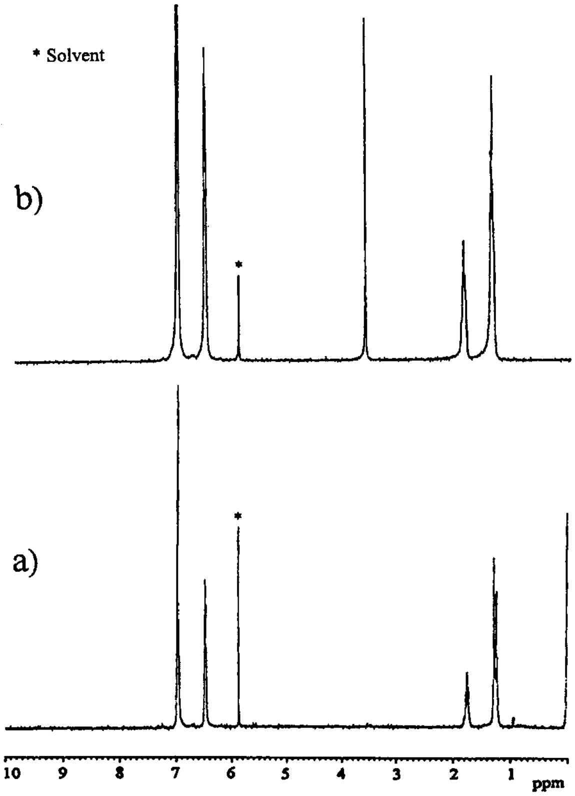


Figure 3. ^{1}H NMR spectra of (a) the starting *s*-PS-*t*-OH ($M_n = 50 \times 10^3$ g/mol; $M_w/M_n = 2.5$) and (b) the resulting *s*-PS-*b*-PEO diblock copolymer (solvent: 1,1,2,2-tetrachloroethane-*d*).

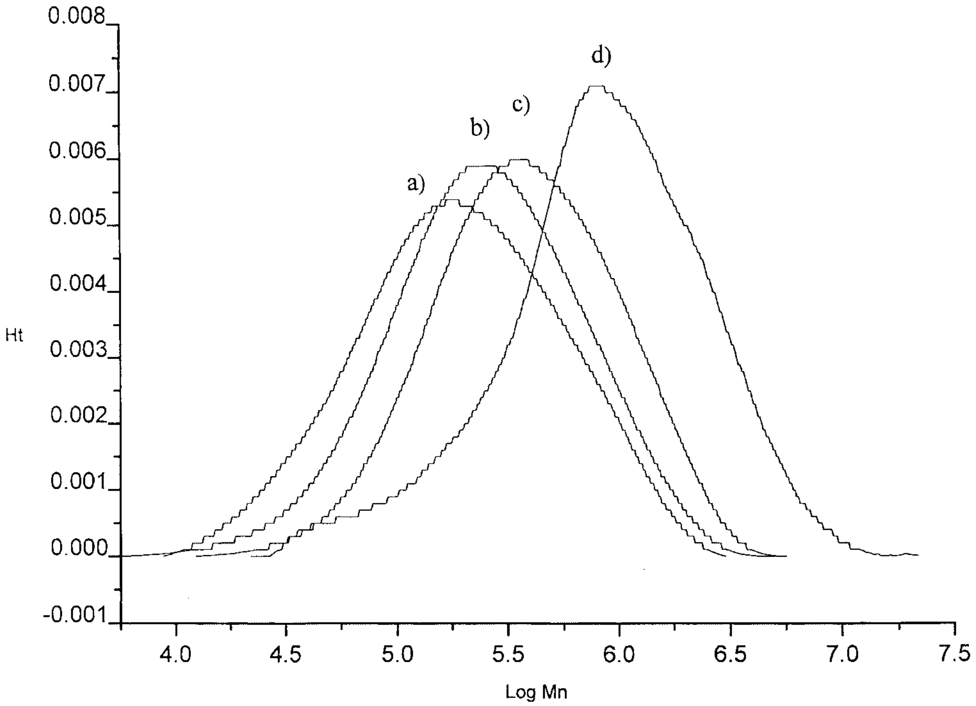


Figure 4. GPC curves of (a) the starting P(E-*co*-O)-*t*-OH copolymer containing 40 mol % 1-octene (M_n = 121 × 10^3 g/mol; M_w/M_n = 2.2) and several corresponding P(E-*co*-O)-*b*-PEO diblock copolymers, including (b) B-1, (c) B-3, and (d) B-5 in Table 2(solvent: THF; temperature: 35 °C).

cess. Ethylene oxide was almost completely incorporated into the diblock copolymer despite the high molecular weight of the starting P(E-*co*-S) polymer. The polymer's molecular weight distribution was maintained at very constant and moderate levels (M_w/M_n < 2.5). The combination of the monochromatic increase of the copolymer molecular weight and the absence of detectable homopolymers clearly points to the existence of a polymeric initiator with an active end group and the living anionic ring-opening polymerization of ethylene oxide during the chain-extension process.

The quantitative copolymer composition was determined by ^{1}H NMR measurement, and the results are summarized in Table 2. Figure 5 compares the ^{1}H NMR spectra of two P(E-*co*-O)-*b*-PEO diblock copolymers (runs B-1 and B-4) with the starting P(E-*co*-O) polymer. In addition to several chemical shifts from the P(E-*co*-O) segment at 0.83, 1.04, 1.20, and 1.31 ppm corresponding to —CH$_2$—**CH**$_3$, —CH$_2$—**CH**—, —**CH**$_2$—**CH**$_2$—, and —**CH**$_2$—CH$_3$, respectively, there is a chemical shift at 3.53 ppm corresponding to the —**CH**$_2$—O— in PEO, which increases its intensity with the amount of ethylene oxide applied. The integrated intensity ratio among the chemical shifts at 1.20, 0.83, and 3.53 ppm determines the mole ratio of [ethylene]/[1-octene]/[ethylene oxide]. In general, the composition of diblock copolymer determined by ^{1}H NMR agrees with the molecular weight estimated from GPC. All the reaction steps, including B–H chain-transfer reaction, active-site transformation, and ring-opening polymerization, must be very effective. The molecular structure of the P(E-*co*-O)-*b*-PEO diblock copolymer can be controlled. The molecular weight of the P(E-*co*-S) block is proportional to the [monomer]/[H–B] ratio during metallocene polymerization, and the molecular weight of PEO is determined by the ethylene oxide monomer feed.

Similar results were also observed in another amorphous P(E-*co*-S) polymer system. Figure 6 compares the ^{1}H NMR spectra of two P(E-*co*-S)-*b*-PEO diblock copolymers (runs C-1 and C-5) with the starting P(E-*co*-S) polymer (M_n = 42 × 10^3 g/mol and M_w/M_n = 2.2). In addition to several chemical shifts from the P(E-*co*-S) segment at 1.20, 1.35, and 6.95–7.15 ppm corresponding to —**CH**$_2$—, —**CH**—, and —C$_6$**H**$_5$, there is a chemical shift at 3.53 ppm (**CH**$_2$—O—) for PEO, which increases its intensity with higher ethylene oxide feed. The integrated intensity ratio among the chemical shifts at 1.35, 6.95–7.15, and 3.53 ppm determines the mole ratio of [ethylene]/[styrene]/[ethylene oxide]. Despite the high starting molecular weight of the P(E-*co*-S) polymer, the chain extension with ethylene oxide under homogeneous conditions was uniform and gave high yields of the block copolymer. In run C-5, the P(E-*co*-S)-*b*-PEO obtained was a high-molecular-weight polymer ($M_n = 106 \times 10^3$ g/mol) with narrow molecular weight distribution ($M_w/M_n = 2.3$) comparable to that ($M_w/M_n = 2.2$) of the starting P(E-*co*-S) polymer.

Figure 7 illustrates two DSC curves of P(E-*co*-O)-*b*-PEO (run B-3) and P(E-*co*-S)-*b*-PEO (run C-5) diblock copolymers that contain nearly equal molar ratios of hydrophobic polyolefin and hydrophilic PEO. Each curve shows only a single T_m peak at ~60 °C for the PEO segment and a glass-transition temperature (T_g) for polyolefin segment. The lowest T_g observed was −62 °C in the P(E-*co*-O) segment containing about 40 mol % of 1-octene units, shown in Figure 7(b). On the other hand, the T_g of the P(E-*co*-S) segment is relatively high (−15 °C) because of the high T_g of PS. The single T_g with a sharp thermal transition in the diblock copolymer is almost identical to that of the starting P(E-*co*-O) or P(E-*co*-S) polymer, which indicates not only the random polyolefin copolymer structure but also the clear phase separation between the hydrophobic polyolefin and the hydrophilic PEO domains.

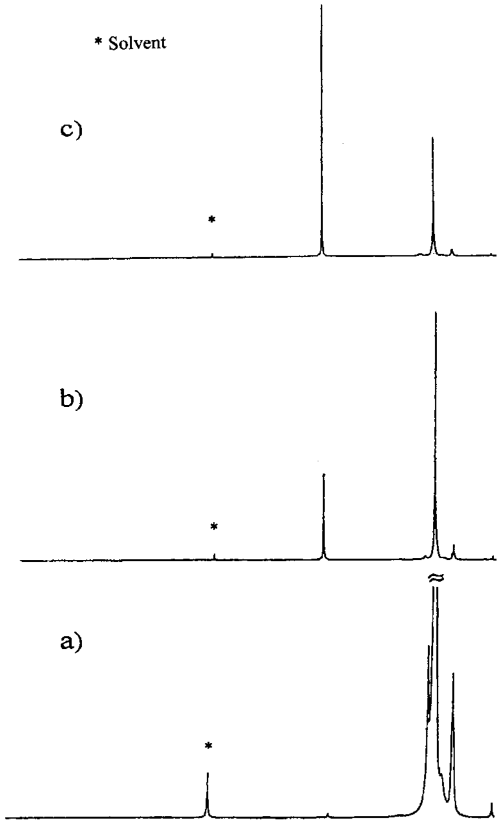


Figure 5. ^{1}H NMR spectra of (a) the starting P(E-*co*-O)-*t*-OH copolymer containing 40 mol % 1-octene ($M_n = 121 \times 10^3$ g/mol; $M_w/M_n = 2.2$) and the resulting P(E-*co*-O)-*b*-PEO diblock copolymers, including (b) B-1 and (c) B-4 in Table 2 (solvent: 1,1,2,2-tetrachloroethane-*d*).

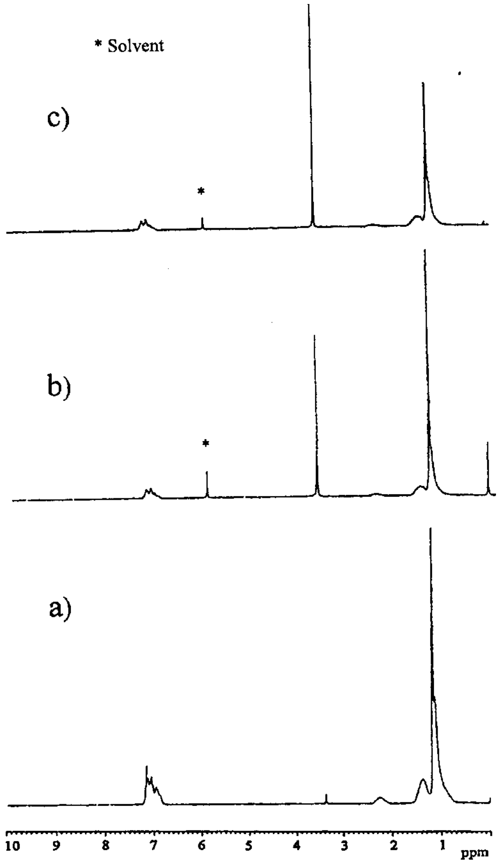


Figure 6. ^{1}H NMR spectra of (a) the starting P(E-*co*-S)-*t*-OH copolymer containing 30 mol % styrene ($M_n = 42 \times 10^3$ g/mol and $M_w/M_n = 2.2$) and several corresponding P(E-*co*-S)-*b*-PEO diblock copolymers, including (b) C-1 and (c) C-5 in Table 2 (solvent: 1,1,2,2-tetrachloroethane-*d*).

PE/PEO Polymer Blends

It is interesting to investigate the compatibility of PE-*g*-PEO diblock copolymer in two very incompatible high-density polyethylene (HDPE) and PEO blends. Two polymer blends are compared;

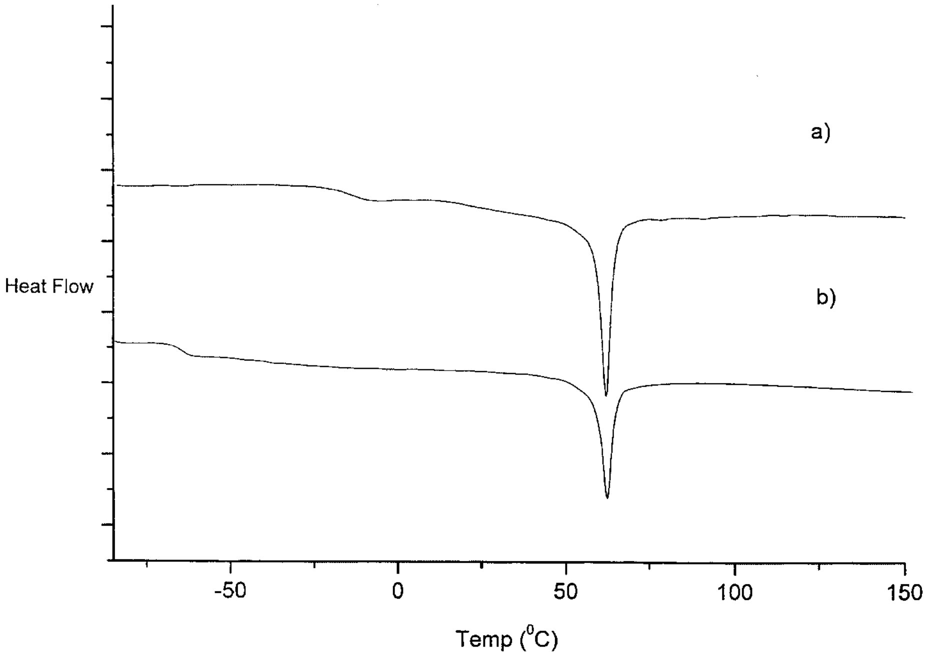


Figure 7. DSC curves of (a) P(E-*co*-S)-*b*-PEO with 58.2 mol % ethylene oxide (C-5) and (b) P(E-*co*-O)-*b*-PEO with 53.5 mol % ethylene oxide (B-3) (second heating cycle with the heating rate 20 °C/min).

one is a simple mixture of 75/25 between HDPE and PEO, and the other features an additional 10 wt % of PE-*b*-PEO (PE/PEO~1/1 mole ratio) in the PE/PEO blend. Figure 8 displays the SEM micrographs, operating with secondary electron imaging, that show the surface topography of cold fractured-film edges. The films were cryro-fractured in liquid N_2 to obtain an undistorted view representative of the bulk material.

In the homopolymer blend, the polymers are grossly phase separated, as can be seen by the PEO component that exhibits poorly dispersed domains and voids at the fracture surface [as shown in Figure 8(a)]. This “ball and socket” topography is indicative of poor interfacial adhesion between the HDPE and PEO domains and represents some PEO domains that are pulled out of the HDPE matrix. Such pullout indicates that limited stress transfer takes place between the phases during fracture. A similar blend containing the PE-*b*-PEO diblock copolymer exhibits a very different morphology [Fig. 8(b)]. The material exhibits no distinct PEO phases, indicating that fracture occurred through both phases or that the PEO phase domains are too small to be observed. The PE-*b*-PEO is an effective compatibilizer in this hydrophobic/hydrophilic blend and warrants further exploration.

CONCLUSIONS

The combination of an *in situ* B–H chain-transfer reaction during the metallocene-mediated olefin polymerization and the subsequent chain extension of ethylene oxide by ring-opening polymerization presents a very convenient route for preparing new amphiphilic diblock copolymers containing PEO and polyolefin blocks. The generality of this chemistry allows a broad choice of polyolefin blocks, covering a range of polyolefin homo- and copolymers from high T_m thermoplastics to low T_g elastomers. The chain-extension reaction of ethylene oxide from the polymeric initiator is generally effective, except in the cases involving high-molecular-weight and highly crystalline polyolefin homopolymers. Under the proper reaction conditions, the chemistry produces amphiphilic diblock copolymers with good control of molecular structure in terms of molecular weight, molecular weight distribution, and balance between hydrophobicity and hydrophilicity. In polymer blends, the incompatibility between PE and PEO polymers was altered by the addition of a small percentage of a PE-*b*-PEO copolymer, as evidenced by the improved dispersion of PEO in the PE matrix and increased interfacial interactions.

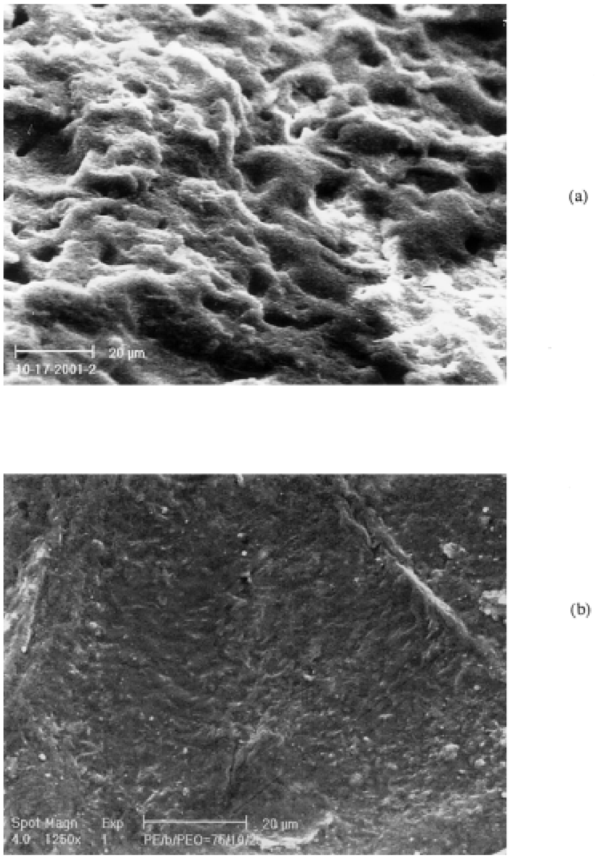


Figure 8. SEM micrographs of polymer blends: (a) two homopolymer blends with PE/PEO = 75/25 and (b) two homopolymers and PE-*b*-PEO with PE/PE-*b*-PEO/PEO = 75/10/25 (1250×).

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