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Syntheses of diblock copolymers polyolefin-*b*-poly(ε-caprolactone) and their applications as the polymeric compatilizer

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Abstract

An effective route to synthesize the amphiphilic diblock copolymer containing a poly(ε-caprolactone) block and a polyolefin block, such as polyethylene, syndiotactic polystyrene and isotactic polypropylene is discussed in this article. There are two reaction steps including the preparation of polyolefins by the combination of metallocene/methylaluminoxane as catalyst system and various chain transfer agents as well as the subsequent anionic ring-opening polymerization of ε-caprolactone. The molecular structure in terms of composition, molecular weight, molecular weight distribution of the diblock copolymers prepared is controllable by these well-defined reaction mechanisms. The scanning electron microscope (SEM) results showes that the compatibilities of the polyolefins and polycarbonate blends are improved greatly using these amphiphilic diblock copolymers as the polymeric compatilizers.

Keywords: Polyolefin-*b*-poly(ε-caprolactone); Amphiphilic diblock copolymer; Polymer blends

1. Introduction

Amphiphilic copolymers with both hydrophilic and hydrophobic polymer chains in one copolymer have attracted great attention for a long time because of their interesting surface properties [1]. They are mainly used as the surfactant, such as dispersants, emulsifiers, stabilizers, antifoaming agents in aqueous solution, surface modifiers for plastics and compatilizers in polymer blends and composites [2–6]. The precise control of the copolymer structure including molecular weight, molecular weight distribution and composition is the key issue considering its application as surfactant. Poly(ε-caprolactone) (PCL), prepared by anionic ring-opening polymerization of ε-caprolactone, is one of the hydrophilic polymers which is safe, biocompatible, biodegradable and widely used in the biomedicine field [7]. Polyolefin is usually prepared from a transition-metal coordination polymerization mechanism with Ziegler–Natta and metallocene catalysis, especially the ones prepared by metallocene catalysis has well-defined molecular weight and compositional distributions. There are two preferred methods in the synthesis of PCL-based copolymers including sequential ring-opening polymerization, used in the preparation of PLLA/PCL [8], PCL/PDMS [9], PCL/Poly(tetrahydrofuran) [10] block copolymers and chain extension involving anionic ring-opening polymerization of ε-caprolactone from a side chain functionalized polyolefins [11,12]. And there are also other reports concerning the syntheses of diblock copolymers with different hydrophilic and hydrophobic blocks [13–15]. So far there is no amphiphilic diblock copolymer having poly(ε-caprolactone) and polyolefin reported in the literature.

An effective route to synthesize the amphiphilic diblock copolymer containing a poly(ε-caprolactone) block and a polyolefin block including polyethylene, syndiotactic polystyrene and isotactic polypropylene with well-controlled molecular structure is discussed in this article. This process resembles a transformation reaction from metallocene-mediated olefin polymerization in the presence of chain transfer agent to anionic ring-opening polymerization

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of ε-caprolactone via a modified terminal group as the macromolecular initiator.

The potential application of this kind of diblock copolymer is as the polymeric compatizer in the polymer blends and the addition of the functional polymer PCL with low melting point will improve the toughness and processing property of the polyolefins such as PE, sPS and iPP. The dyeability, printability and the compatibility with other materials of the polyolefins are also altered by the addition of functional polymer. It is interesting to investigate the compatibility of the diblock copolymers containing a polyolefin block and a poly(ε-caprolactone) block in two very incompatible polyolefin and functional polymer such as poly(ε-caprolactone) (PCL) and polycarbonate (PC). The SEM results of polymer blends show that the compatibilities between polyolefins (PE, sPS and iPP) and functional polymer (PCL, PC) are greatly enhanced by the addition of prepared diblock copolymers as polymeric compatizer.

2. Experimental work

2.1. Materials

Toluene and hexane were dried by stirring with sodium and benzophenone under argon and distilled out before use. $B(C_6F_5)_3$ (Aldrich) was sublimated before use. High-purity-grade ethylene and propylene (MG Industries), ε-caprolactone (Aldrich 99+%), methanol, $Al(C_2H_5)_2Cl$ (1.8 mol/L solution in toluene), 9-BBN, polyethylene ($M_w = 1.25 \times 10^5$ g/mol), poly(ε-caprolactone) ($M_w = 6.5 \times 10^4$ g/mol), isotactic polypropylene ($M_w = 8.0 \times 10^4$ g/mol) and polycarbonate ($M_w = 2.9 \times 10^4$ g/mol) were purchased and used as received. Syndiotactic polystyrene was prepared according to the reference and its weight-average molecular weight was $M_w = 1.50 \times 10^5$ g/mol by GPC. 4-(*tert*-Butyldimethylsilyloxy)styrene was synthesized according to Ref. [16]. The metallocene catalysts, including $[Cp_2^*ZrMe]^+[MeB(C_6F_5)_3]^-$, $[Cp^*TiMe_2]^+[MeB(C_6F_5)_3]^-$ and *rac*-$Me_2Si[2\text{-}Me\text{-}4\text{-}Ph(Ind)]_2ZrCl_2$ were prepared by the published procedures [17–19].

2.2. Synthesis of terminal functionalized polyethylene and syndiotactic polystyrene

The borane terminated polyethylene (PE-*t*-B) and the syndiotactic polystyrene (sPS-*t*-B) were prepared by $[Cp_2^*ZrMe]^+[MeB(C_6F_5)_3]^-$ and $[Cp^*TiMe_2]^+[MeB(C_6F_5)_3]^-$, respectively. The oxidation of the borane terminal group is very effective under the moderate reaction conditions to obtain PE-*t*-OH and sPS-*t*-OH. The detailed experimental procedures were described in the literature [20–22].

The subsequent metallation reactions were carried out in toluene at 100 °C. In a typical example, a 100 mL flask equipped with the stirrer was charged with 2.0 g dry PE-*t*-OH (number average molecular weight (M_n) = 10×10^3 g/mol; molecular weight distribution ($M_w/M_n = 2.2$)) and purged with argon. 30 mL dry, O_2 free toluene was injected to the flask and the mixture was stirred at 100 °C for 5 h in order to well resolve the polymer. After the injection of 1.0 mL $Al(C_2H_5)_2Cl$ (1.8 mol/L solution in toluene) into the mixture, the reaction system was stirred at 100 °C for 8 h and cooled down to room temperature. Under the protection of argon, the suspension was filtered and washed with dry hexane for 3 times to remove the unreacted $Al(C_2H_5)_2Cl$ and the polymer solid was dried under vacuum at 60 °C for 2 h. The resulting metallated polymer PE-*t*-$OAl(C_2H_5)_2$ or sPS-*t*-$OAl(C_2H_5)_2$ was used directly in the subsequent ring-opening polymerization.

2.3. Synthesis of terminal functionalized isotactic polypropylene

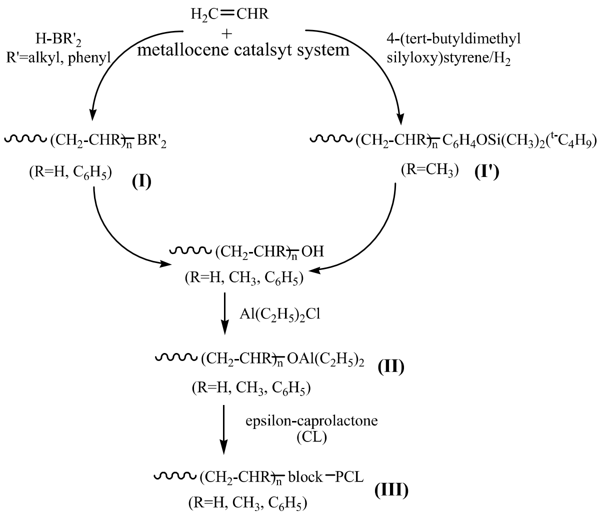
The hydroxyl group terminated isotactic polypropylene (iPP-*t*-OH) was prepared by *rac*-$Me_2Si[2\text{-}Me\text{-}4\text{-}Ph(Ind)]_2ZrCl_2$/MAO catalyst system with 4-(*tert*-butyldimethylsilyloxy)styrene/H_2 as the chain transfer agent according to the reference [23]. And the metallation reaction was the same as that of polyethylene system discussed above.

2.4. Synthesis of polyolefin-b-poly(ε-caprolactone) diblock copolymer

The anionic ring opening polymerization was carried out in toluene at 100 °C for 24 h. In the drybox, the metallated polymer (2.0 g) was mixed with desired quantity of ε-caprolactone and 30 mL dry toluene in a 100 mL flask. After stirring at 100 °C for 24 h, the polymerization reaction was terminated with acidified methanol. The precipitated polymer was washed with methanol several times and dried under vacuum at 60 °C for 8 h. The copolymer was then extracted with boiling acetone for 48 h to remove the poly(ε-caprolactone) homopolymer which was caused by the interesterification reaction.

2.5. Characterization

All ^1H 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 molecular weight distribution of the polymers were determined by gel permeation chromatography (GPC) with a Waters GPC 600E equipped by 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 0.7 mL/min was used and the mobile phase was 1,3,5-trichlorobenzene at 140 °C with PS as standard for calibration. Differential scanning calorimetry (DSC) was performed on a Perkin–Elmer 7 Series thermal analysis system at the



Scheme 1. Scheme of the transformation from metallocene-mediated polymerization to anionic ring-opening polymerization.

second scanning with the rate of 20 °C/min. Scanning electron microscopy (SEM) was used to view some fractured interface of the polymer blend films with a Topcon International Scientific Instruments ISI-SX-40 using secondary electron imaging.

2.6. Polymer blending

The polymer blends with desired compositions were prepared by the Brabender PL2000 Plastic-Corder under the protection of argon at desired temperature. SEM samples were prepared from films cryo-fractured in liquid nitrogen. Samples were mounted on an aluminum stub and gold coated to form a conductive coating.

3. Results and discussion

A new synthesis route to preparing a range of amphiphilic diblock copolymers containing a PCL bock and a polyolefin block is discussed in this article. Scheme 1 illustrates the polymerization scheme that is focused on the transformation from metallocene polymerization of olefin to anionic ring-opening polymerization of ε-caprolactone via a metalated terminal group. In the presence of a dialkylborane ($H–BR_2$) as chain transfer agent for ethylene and styrene polymerization system or 4-(*tert*-butyldimethylsilyloxy)-styrene/H_2 as chain transfer agents for polymerization of propylene, the metallocene-mediated propagating polyolefin chain engages in a facile ligand exchange reaction to form a borane (**I**) or 4-(*tert*-butyldimethylsilyloxy)styrene (**I**′) terminated polyolefin with a narrow molecular weight distribution. The molecular weight of the prepared polyolefin is proportional to the molar ratio of [chain transfer agent]/[olefin]. The terminal group is then transformed to an anionic initiator for ε-caprolactone polymerization by oxidation of borane to a hydroxyl group using $NaOH/H_2O_2$ reagent or by acidification of *tert*-butyldimethylsilyloxy group to a hydroxyl group using acidified methanol, and subsequent metallation of the terminal OH group with diethyl aluminum chloride to achieve an initiator at the polyolefin chain end (**II**), which is active for the anionic ring-opening polymerization of ε-caprolactone to form the resulting diblock copolymer (**III**).

The experimental results of the diblock copolymers containing polyolefins including PE, sPS, iPP and functional polymer (PCL) are summarized in Table 1. They were prepared by terminal metalated polyethylene (PE-*t*-$OAl(C_2H_5)_2$), syndiotactic polystyrene (sPS-*t*-$OAl(C_2H_5)_2$)

Table 1
Summary of PE-*b*-PCL, sPS-*b*-PCL and iPP-*b*-PCL diblock copolymers

Run	Polymeric initiator			ε-CL (mL)	Product (g)		ε-CL Incrop.[a] mol %	M_n of copolymer[b] (10^3 g/mol)
	Kind	g	M_n[c] (10^{-3} g/mol)		Soluble part in acetone	Insoluble part in acetone		
A1	PE-*t*-$OAl(C_2H_5)_2$	2.0	10	2.0	0.4	3.0	11.8	15
A2	PE-*t*-$OAl(C_2H_5)_2$	2.0	10	3.0	0.7	4.1	20.4	20
A3	PE-*t*-$OAl(C_2H_5)_2$	2.0	10	5.0	0.9	5.8	32.0	29
A4	PE-*t*-$OAl(C_2H_5)_2$	2.0	10	7.0	1.6	6.7	36.8	34
A5	PE-*t*-$OAl(C_2H_5)_2$	2.0	10	9.0	2.8	7.5	40.2	37
A6	PE-*t*-$OAl(C_2H_5)_2$	1.0	54	4.0	1.7	3.2	41.0	207
A7	PE-*t*-$OAl(C_2H_5)_2$	1.0	77	4.0	1.1	2.7	29.4	207
A8	PE-*t*-$OAl(C_2H_5)_2$	1.0	124	4.0	0.7	1.3	7.19	163
B1	sPS-*t*-$OAl(C_2H_5)_2$	0.5	25	1.0	0.4	0.84	37.9	96
B2	sPS-*t*-$OAl(C_2H_5)_2$	0.5	25	3.0	0.9	1.3	61.1	185
C1	iPP-*t*-$OAl(C_2H_5)_2$	1.0	12	5.0	1.4	4.4	55.8	53
C2	iPP-*t*-$OAl(C_2H_5)_2$	1.0	50	5.0	1.2	3.7	50.2	187

Conditions: Solvent, 30 mL toluene; reaction temperature, 100 °C; reaction time, 24 h.

[a] Determined by ^1H NMR.

[b] Calculated by ^1H NMR.

[c] By GPC in 1,3,5 trichlorobenzene at 140 °C with PS as standard.

and isotactic polypropylene (iPP-*t*-OAl$(C_2H_5)_2$) prepared from metallocene-mediated polymerization in the presence of chain transfer agent.

In order to estimate the efficiency of the end-group transformation, ^{1}H NMR measurements of PE-*t*-OH and its corresponding metalated product PE-*t*-OAl$(C_2H_5)_2$ have been done under high temperature. As shown in Fig. 1, after the reaction with $Al(C_2H_5)_2Cl$, the chemical shift of methylene connected to hydroxyl group $–CH_2OH$ of PE-*t*-OH disappears, and there are new peaks at 4.0, 1.7 and 0.26 ppm corresponding to the methylene group connected to oxygen atom $–CH_2–O–Al–$, methylene group connected to aluminum atom $–O–Al–(CH_2CH_3)_2$ and end methyl groups $–O–Al–(CH_2CH_3)_2$, respectively. It indicates that the efficiency of end-group transition is high, the reaction between PE-*t*-OH and $Al(C_2H_5)_2Cl$ is totally completed.

Fig. 2 shows the ^{1}H NMR spectra of two PE-*b*-PCL copolymers (run A2 and run A6), which have been prepared by the PE-*t*-OAl$(C_2H_5)_2$ polymers with different molecular weights, sPS-*b*-PCL diblock copolymer (run B1) as well as iPP-*b*-PCL diblock copolymer (run C1). Besides the peak at 1.30 ppm for $–CH_2–CH_2–$ units of PE, several new peaks at 4.1, 3.7, 2.3, 1.7 and 1.5 ppm corresponding to the methylene group connected to oxygen atom $–CH_2–CH_2–O–$, methylene group at the chain end $–CH_2–OH$, methylene group connected to the carbonyl $–C(=O)–CH_2–$, the two kinds of methylene group $–CH_2–$ ($\beta\gamma'$) and ($\gamma\gamma$) on the backbone of PCL, respectively, increase their intensity with the increasing quantity of ε-caprolactone. The intensity ratio

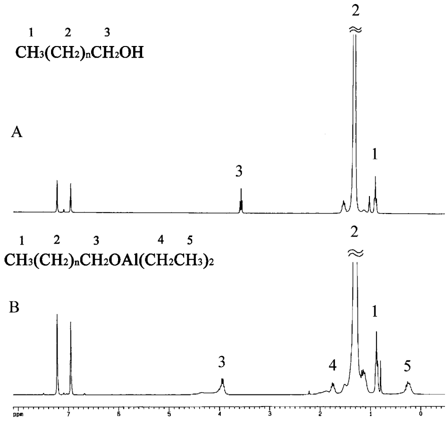


Fig. 1. ^{1}H NMR spectra of PE-*t*-OH and PE-*t*-OAl$(C_2H_5)_2$.

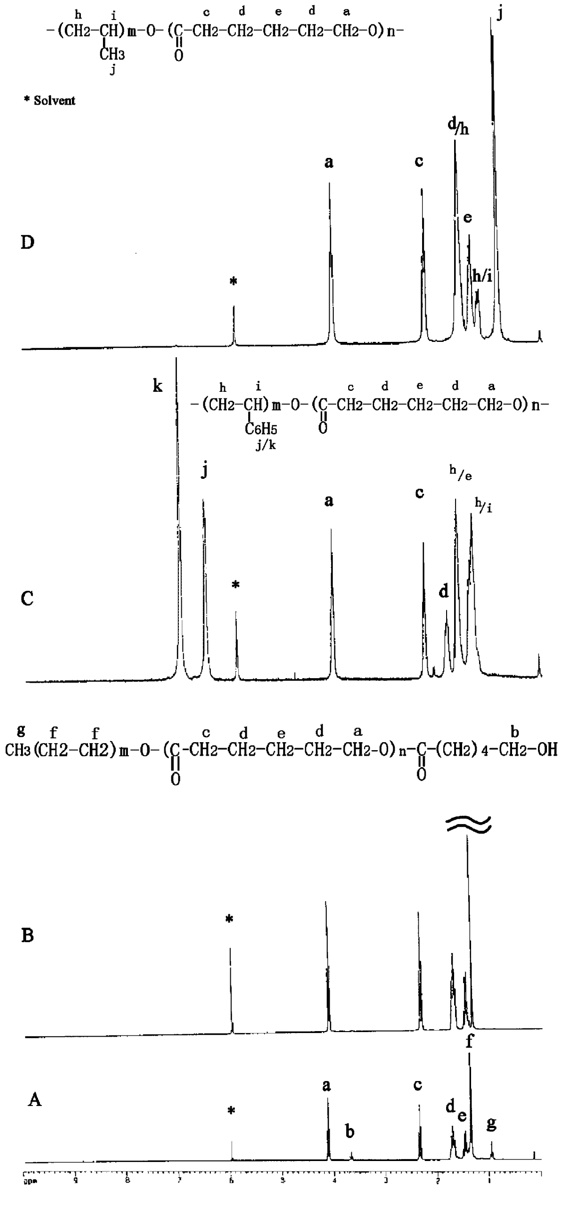


Fig. 2. ^{1}H NMR spectra of diblock copolymers (A) PE-*b*-PCL (run A2); (B) PE-*b*-PCL (run A6); (C) sPS-*b*-PCL (run B1) and (D) iPP-*b*-PCL (run C1).

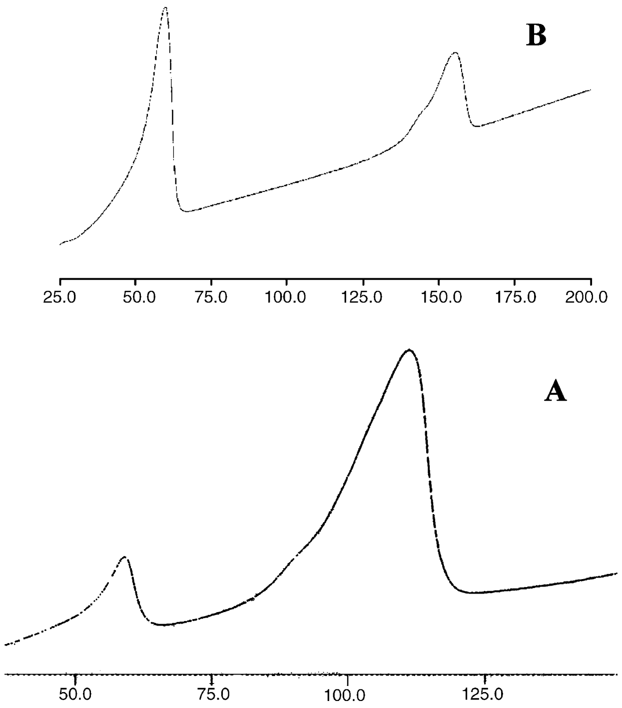


Fig. 3. DSC curves of diblock copolymers (A) PE-*b*-PCL (run A1) and (B) iPP-*b*-PCL (run C1).

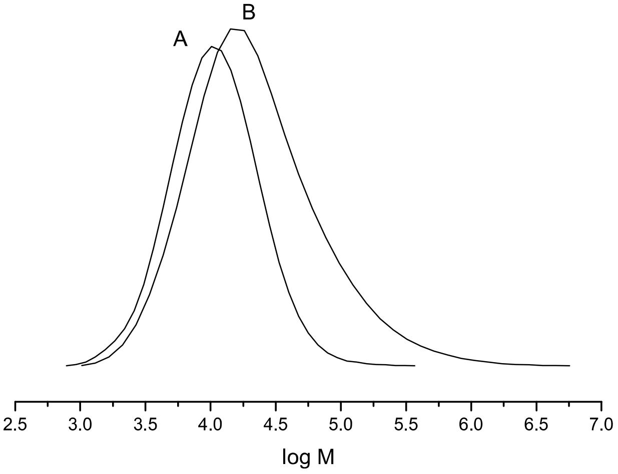


Fig. 4. GPC curves of (a) PE-*t*-OH and (b) diblock copolymer PE-*b*-PCL (run A1).

between 1.30 and 4.1 ppm is used to determine the mole ratio of [ethylene]/[ε-caprolactone] in the diblock copolymer. Although there is some poly(ε-caprolactone) homopolymer isolated from solvent extraction of the resulting diblock copolymer which is caused by the interesterification, the poly(ε-caprolactone) block continuously grows with the supply of ε-caprolactone monomer. A high molecular weight PE-*b*-PCL diblock copolymer with up to 41 mol% of PCL content [Fig. 2(B)] is obtained. Under the described reaction conditions, the molecular weight of polyethylene does not affect the subsequent ring-opening polymerization of ε-caprolactone greatly due to the good solubility of polyethylene in toluene at elevated temperature. But with the increasing of the molecular weight of polyethylene, the transformation reaction and anionic ring opening polymerization are limited by the availability of end groups due to the reduced solubility of the polyolefin in toluene. The molar ratio between [styrene]/[ε-caprolactone] of sPS-*b*-PCL diblock copolymer is determined by the intensity ratio between 6.95 and 7.15 ppm corresponding to $-C_6H_5-$ unit of sPS and 4.1 ppm corresponding to methylene group $-CH_2-$ of PCL [Fig. 2(C)]. The intensity ratio between 0.9 ppm corresponding to methyl group of iPP and 4.1 ppm corresponding to methylene group $-CH_2-$ of PCL was used to determine the molar ratio of [propylene]/[ε-caprolactone] [Fig. 2(D)].

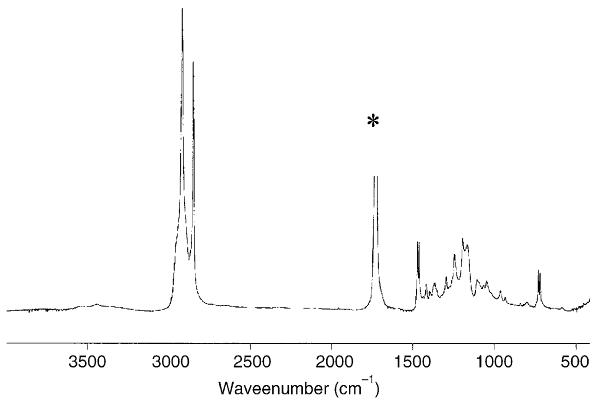


Fig. 5. FTIR spectrum of diblock copolymer PE-*b*-PCL (run A2).

Table 2
Polymer blends composition and the blending conditions

Run	Composition	Weight ratio	Blending temperature (°C)
D1	PE/PCL	75/25	165
D2	PE/PE-*b*-PCL/PCL	75/10/25	165
E1	PE/PC	75/25	290
E2	PE/PE-*b*-PCL/PC	75/10/25	290
F1	iPP/PC	75/25	290
F2	iPP/iPP-*b*-PCL/PC	75/10/25	290
G1	sPS/PC	75/25	300
G2	sPS/sPS-*b*-PCL/PC	75/10/25	300

Blending the polymer mixture for 10 min under the protection of argon.

Two distinctive melting endothermal peaks are observed for each diblock copolymer indicating a clear phase separation between the hydrophobic and hydrophilic domains shown in Fig. 3. Fig. 4 compares the GPC curves of original PE-*t*-OH and the diblock copolymer PE-*b*-PCL (run A1) after the purification by solvent extraction. There is no obvious bimodal peak in curve B, which means the composition distribution of the diblock copolymer is uniform, and no homopolymers can be detected with

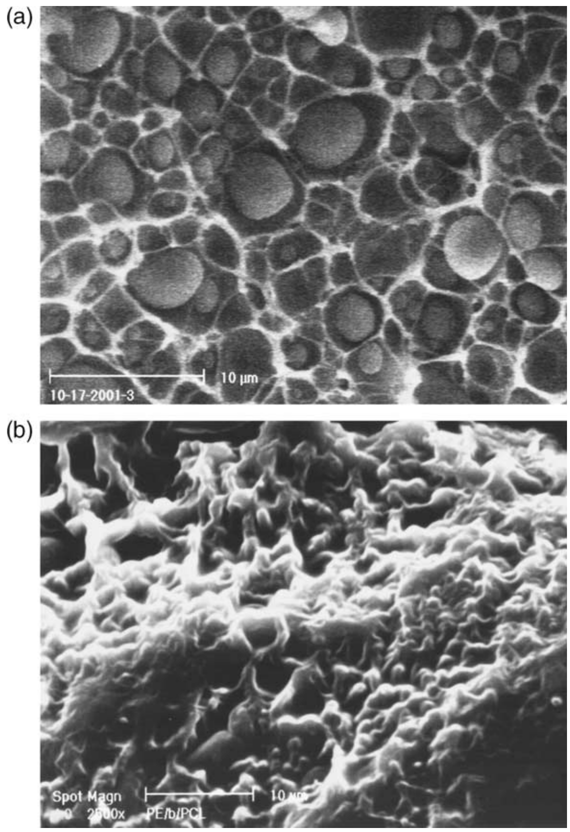


Fig. 6. SEM micrographs of polymer blends: (a) Two homopolymer blends with PE/PCL = 75/25 and (b) two homopolymers and PE-*b*-PCL with PE/PE-*b*-PCL/PCL = 75/10/25 (2500×).

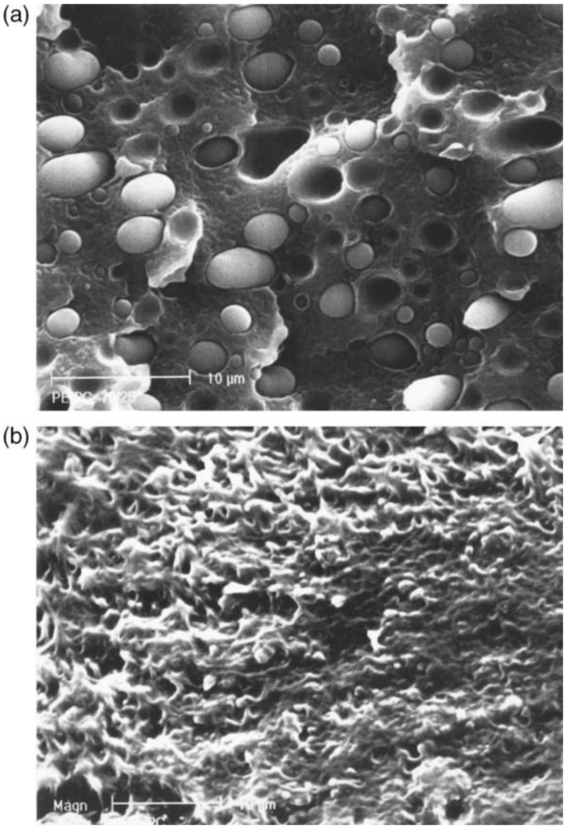


Fig. 7. SEM micrographs of polymer blends: (a) Two homopolymer blends with PE/PC = 75/25 and (b) two homopolymers and PE-*b*-PCL with PE/PE-*b*-PCL/PC = 75/10/25 (2500×).

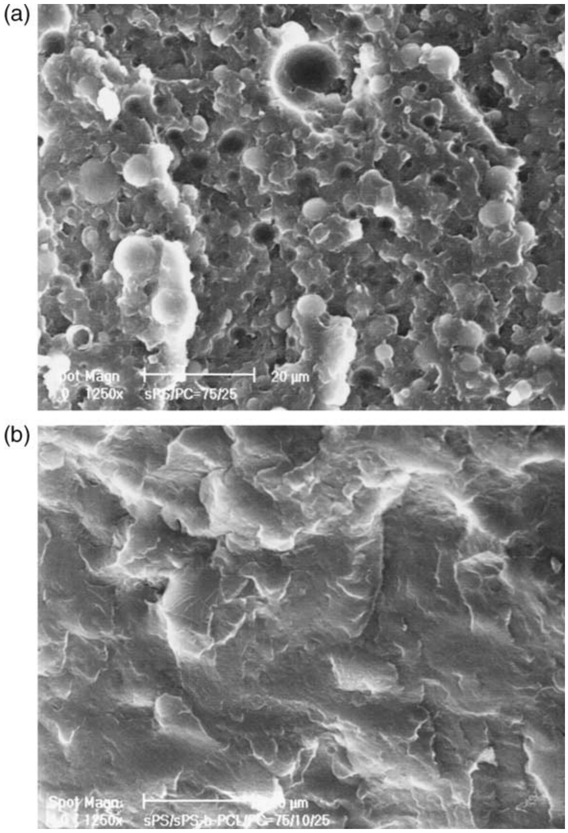


Fig. 8. SEM micrographs of polymer blends: (a) Two homopolymer blends with sPS/PC = 75/25 and (b) two homopolymers and sPS-*b*-PCL with sPS/sPS-*b*-PCL/PC = 75/10/25 (1250×).

relatively low molecular weight PE-*t*-OH. Fig. 5 depicts the FTIR spectrum of diblock copolymer PE-*b*-PCL (run A2) with 20.4 mol% of PCL content. The peak at 1724 cm^{-1} is derived from the vibration absorption of carbonyl group in the backbone of PCL.

One of the applications of such amphiphilic diblock copolymers is as the compatilizer in polymer blends and composite materials. Four pairs of polymer blends are compared with one mixture of 75/25 (weight ratio) between polyolefin and functional polymer, and another features an additional 10 wt% of diblock copolymer as compatilizer in each set. The experimental conditions for the preparation of polymer blends are summarized in Table 2. Figs. 6–9 display the SEM micrographs, operating with secondary electron imagings, which show the surface topography of cold fractured film edges. The films were cryo-fractured in liquid nitrogen to obtain an undistorted view representative of the bulk material.

In the polyethylene homopolymer blends, the polymers are grossly phase separated, as can be seen by the PCL or PC component that exhibits poorly dispersed domains and voids at the fracture surface (shown in Figs. 6(a) and 7(a)). The 'ball and socket' topography with big size obviously represents that some PCL or PC domains are pulled out of the PE matrix. Such pullout indicates that limited stress transfer takes place between the phases during fracture. The interface boundary between PE and PCL or PC is clearly seen because the adhesion of the two homopolymers is poor. A similar blend containing the PE-*b*-PCL diblock copolymer exhibits very small PCL or PC phases and some plastic deformation, indicating that the sizes of PCL or PC phase domains are reduced greatly comparing that of the homopolymer blends and the adhesion between both phases increases very much. The result shows that PE-*b*-PCL is an effective compatilizer in these hydrophobic/hydrophilic blends.

In general, similar results were also observed in other polymer blend systems. Figs. 8 and 9 compare the SEM micrographs of sPS/PC and iPP/PC homopolymer blends with or without diblock copolymer as compatilizers. Comparing the size of PC domains in the sPS or iPP matrix, the compatibility of the hydrophilic/hydrophobic polymer blends sPS/PC or iPP/PC are enhanced obviously by the addition of sPS-*b*-PCL or iPP-*b*-PCL diblock copolymer as compatilizers, respectively. These diblock copolymers containing a polyolefin block and a poly(ε-caprolactone) block are effective compatilizers in the hydrophilic/hydrophobic polymer blends between polyolefins and functional polymers and warrant further exploration.

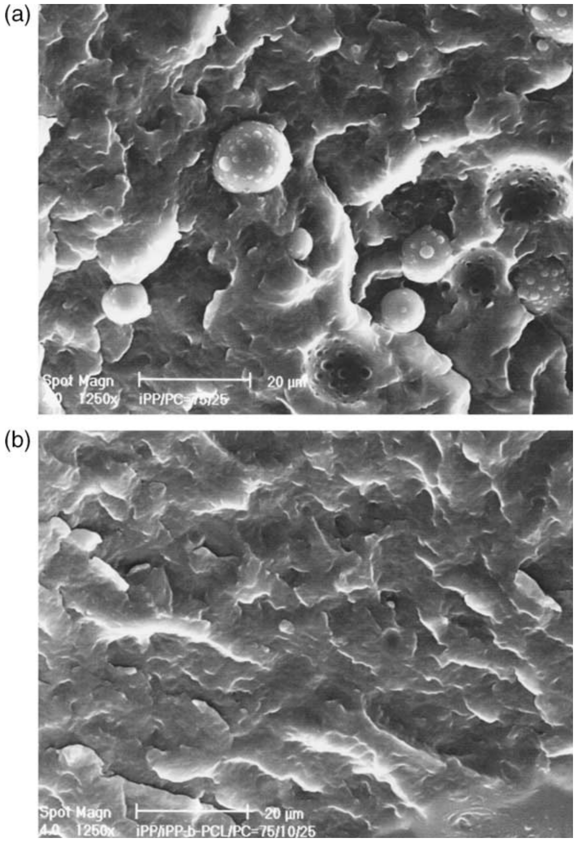


Fig. 9. SEM micrographs of polymer blends: (a) Two homopolymer blends with iPP/PC = 75/25 and (b) two homopolymers and iPP-*b*-PCL with iPP/iPP-*b*-PCL/PC = 75/10/25 (1250×).

4. Conclusions

A convenient route for synthesis of new amphiphilic diblock copolymers containing PCL and polyolefin blocks is studied by the transformation from metallocene-mediated polymerization of olefins in the presence of various chain transfer agents to the anionic ring-opening polymerization of ε-caprolactone monomer. This chemistry strategy affords an effective way for the chain extension reaction of ε-caprolactone from the polymeric initiators even in the cases involving high molecular weight and highly crystalline polyolefin homopolymers. Under the moderate conditions, molecular weight, molecular weight distribution and the molecular structure of the prepared amphiphilic diblock copolymers can be well controlled. The improved dispersion of functional polymer in the polyolefins matrix and increased interfacial interactions by SEM indicate that the compatibility between hydrophobic polyolefins and hydrophilic functional polymers, such as PCL and PC, are greatly enhanced by the addition of produced diblock copolymers as compatilizer.

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