

Polyethylene-*b*-poly(ethylene glycol) diblock copolymers: New synthetic strategy and application

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ABSTRACT: Polyethylene-*b*-poly (ethylene glycol) (PE-*b*-PEG) was successfully synthesized by a coupling reaction of hydroxyl-terminated polyethylene (PE-OH) and isocyanate-terminated poly (ethylene glycol) (PEG-NCO). PE-OH was prepared by coordination chain transfer polymerization (CCTP) using 2,6-bis[1-(2,6-diisopropylphenyl)imino ethyl] pyridine iron (II) dichloride /dry ethylaluminumoxane (DEAO) /diethyl zinc (ZnEt₂) as catalyst and subsequent *in situ* oxidation with oxygen. The active centers of this catalyst system were counted, indicating that the active centers were more stable using DEAO as cocatalyst than using dry methylaluminumoxane (DMAO) as cocatalyst. PEG-NCO was synthesized through the condensation reaction of monomethylpoly(ethylene glycol) (PEG) with isophoronediiisocyanate (IPDI). Subsequently, the thermal characterization, morphological characterization and the application of these diblock copolymers was investigated. The results indicated that the diblock copolymers were effective compatilizers for polyethylene/poly(ethylene glycol) blends. Meanwhile, they were excellent surface modification agents for polyethylene membrane and glass sheet, it can efficiently turn a hydrophobic surface into a hydrophilic surface, or vice versa. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42236.

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INTRODUCTION

Block copolymer is not only the key focus areas of contemporary macromolecular chemistry and physics but also grip many immediate commercial applications.¹ In recent years, a new method for the synthesis polyolefins-based block copolymers had attracted increasing interest because it affords a convenient and efficient method for the synthesis of block copolymers with narrow polydispersities and controllable molecular weight.^{2–4} This method is a cascade polymerization process with living coordinative chain-transfer polymerization (CCTP) by using several catalyst systems^{5–16} being the first step to give a polyolefin half-product bearing a terminal reactive group which, after the terminal reactive group is converted to a living polymerization initiator moiety, becomes a macroinitiator leading to the second step polymerization such as atom transfer radical polymerization (ATRP),^{17–20} reversible addition-fragmentation chain transfer polymerization (RAFT),^{21–24} ring-opening polymerization (ROP),^{25–28} Diels-Alder reactions,²⁹ or click coupling reaction^{21,22,30} to obtain diblock copolymers.

The limitation of these catalyst systems is either high cost of the catalyst or the low molecular weight of the resulting PE. Since the linear PE formed in the reactions possess both high crystal-

linity and poor solubility in the solvent at the reaction temperature, the polymers separate from the polymerization media. The polymerization became uncontrollable after a certain conversion is reached. So to obtain PE with high enough molecular weight in a large scale, ethylene polymerization should be catalyzed by a low cost catalyst system at high temperature. Besides, those diblock copolymers prepared by ATRP, RAFT, Diels-Alder reactions, or click chemistry could not be easily industrialized.

PE-*b*-PEG is a typical double-crystalline diblock copolymer, which presents high chain regularity, strong immiscibility, and controlled molecular weights. So it was an ideal model compound to study the crystallization, phase behaviors, and self-assembled structures in the melt or in the solution.^{28,30,31} But few study on the diblock copolymers for commercial applications except Shi *et al.*^{32,33} used the diblock copolymers as a modifier to prepare PE/PE-*b*-PEG blend membranes via a thermally induced phase separation (TIPS) process for water filtration and showed excellent properties.

In our work by using dry ethylaluminumoxane (DEAO) as cocatalyst the polymerization temperature can be obviously enhanced to form PE-OH with a higher molecular weight. Then PE-OH successfully reacted with isocyanate-terminated poly(ethylene

glycol) (PEG-NCO) to prepare di-block copolymer containing PE segment via coupling reaction due to high reactivity between $-OH$ and $-NCO$. Thus a simple but high-efficient method for preparation of diblock copolymers PE-*b*-PEG was provided. Also we did some exploration with the diblock copolymers for industrial application such as compatilizer for linear low density polyethylene/poly(ethylene glycol) (LLDPE/PEG) blends and surface modification agent for glass sheet or polyethylene membrane.

EXPERIMENTAL

Materials

Polymerization-grade ethylene and extra-pure-grade nitrogen were purified by passing through columns of 4Å molecular sieves and deoxygenation catalyst. Oxygen (99.6%) was purified by passing through columns of KOH to remove H_2O . Toluene was refluxed and distilled under nitrogen from sodium/benzophenone before use. Dichloromethane was refluxed by calcium hydride and distilled under nitrogen prior to use. $AlEt_3$ and $ZnEt_2$ were purchased from Albemarle Corporation and used as received. Monomethyl poly(ethylene glycol) (PEG, $M_n = 2000$, $M_w/M_n = 1.03$) was purchased from J&K Scientific Ltd. and dried by azeotropic distillation method with toluene. Dibutyltindilaurate (DBTDL) and isoporondiisocyanate (IPDI) were purchased from J&K Scientific Ltd. and used as received. Anhydrous ethyl ether was purchased from Sinopharm Chemical Reagent Co, Ltd. and used as received. 2,6-Bis[1-(2,6-diisopropylphenyl)imino ethyl] pyridine iron (II) dichloride was synthesized according to the literature procedure.³⁴ Ethylaluminumoxane (EAO) was prepared according to a previously reported method.^{35–38} Methylaluminumoxane (MAO) was purchased from Aldrich as a 10 wt % toluene solution. Dry methylaluminumoxane (DMAO) and dry ethylaluminumoxane (DEAO) were prepared according to the literature procedure and then diluted by toluene to 1.0M.¹⁸ LLDPE ($M_n = 1.05 \times 10^5$, $M_w/M_n = 4.8$, mole content of 1-hexene is 3.6%) was prepared by our laboratory with the fourth-generation Ziegler-Natta catalyst.

Synthesis of Hydroxyl-Terminated Polyethylene (PE-OH)

The synthesis of PE-OH via CCTP followed a similar procedure to that previously reported by literatures.¹⁸ A 2,6-bis[1-(2,6-diisopropylphenyl)imino ethyl] pyridine iron (II) dichloride / DMAO(or DEAO) system was used as catalyst. $ZnEt_2$ was used as chain transfer agent at a mole ratio of Fe : Al : Zn = 1 : 1000 : 2000. The pressure of ethylene was maintained at 0.4 MPa. 30 min (or 10 min) later, the polymerization product was oxidized *in-situ* by oxygen at 100°C for 2 h. The resulting mixture was poured into acidic ethanol. The white powder was filtered, washed with copious ethanol and dried under vacuum at 60°C. The product was extracted by heptane to remove the high molecular weight PE without $-OH$ group (the high molecular weight PE produce by active species after CCTP lose control turn to normal polymerization) and then dried under vacuum at 60°C to give pure PE-OH.

Counting of Active Centers

The counting of active centers followed a similar procedure to that previously reported by literatures by our group.⁴⁰ Ethylene polymerizations were performed in a 150 mL Schlenk flask con-

taining about 50 mL of toluene at 50°C or 60°C under N_2 atmosphere. The reagents were added in the order of solvent, co-catalyst, and the catalyst with $[Fe] = 5 \times 10^{-6}$ mol/L and Al/Fe = 1000 (mol/mol). Then ethylene gas of 1 atm pressure was bubbled into the Schlenk flask for 10 min. Then a 2-thiophenecarbonylchloride (TPCC) toluene solution (in TPCC/Al = 2) was injected into the reactor to quench the polymerization and stirred for 5.5 min. Subsequently acidic ethanol was added to decompose the catalyst, and the polymer was precipitated with excess of ethanol.

The quenched polyethylenes were refluxed by ethanol/HCl mixture for 60 min. Then the polymer was isolated, washed, dried and weighed. Each polymer sample was then purified by one dissolution-precipitation operation, extracted with fresh ethanol in a Soxhlet extractor for 12 h, and then dried in vacuum at 60°C for 8 h.

The sulfur content of the quenched polymer was measured in a GLC-200 microcoulometry sulfur analyzer with a lower detection limit of 0.05 ppm (Jiangyan Yinhe Instrument Co., Jiangyan, China). The polymer sample for analysis was solid powder ($2-4 \pm 0.01$ mg), and the average value of three parallel measurements was taken as the sulfur content (S).

The number of active centers ($[C^*]$) was calculated by the formula:

$$[C^*] = S \times m / (3.2 \times 10^6)$$

m was the mass of the quenched polyethylene.

Synthesis of Isocyanate-Terminated Poly(ethylene glycol) (PEG-NCO)

Isocyanate-terminated poly(ethylene glycol) (PEG-NCO) was prepared by reacting monomethyl poly(ethylene glycol) (PEG) with diisocyanate. IPDI ($-NCO : -OH = 20$) and DBTDL (1 wt % relative to polymer) were added to the reactor under a nitrogen atmosphere. PEG was dissolved in CH_2Cl_2 and added dropwise to the stirred IPDI solution at room temperature in 5 h followed by stirred for an additional 3 h. The product was isolated by the dissolution-precipitation technique with CH_2Cl_2 as dissolvent and ethyl ether as precipitant. The white powder was filtered and dried under vacuum at 30°C to give PEG-NCO.

Synthesis of PE-*b*-PEG Diblock Copolymer

The block copolymer was formed by mixing PEG-NCO (1 mmol) and PE-OH at $-NCO : -OH = 1.2$ followed by injection of DBTDL (1 wt % relative to polymer) and 50 mL toluene. The solution was stirred for 24 h at 120°C. After the solvent being removed a light yellow solid was got. The product was extracted by acetone to remove the unreacted PEG and dried under vacuum at 60°C to give PE-*b*-PEG.

Surface Modification

The PE membrane and glass sheet were washed by *n*-hexane, ethanol, and deionized water for three times respectively and then dried in vacuum at 60°C for 8 h. 0.0866 g of PE-*b*-PEG diblock copolymer dissolved in 10 mL toluene (1 wt %). The solution was poured onto a substrate (glass sheet or polyethylene membrane) at 100°C. Then the substrate was spun at

Table I. Polymerization Conditions and Results for CCTP^a

Entry	Cocat.	Temp.	Act. ^b	Low- M_w fraction			High- M_w fraction	
				M_n^c	PDI ^c	wt %	M_n^c	PDI ^c
1	DMAO	30°C	6.5	0.37	1.35	33.1	405.1	4.57
2	DMAO	40°C	4.0	0.47	1.39	74.9	427.5	3.07
3	DMAO	50°C	2.1	0.53	1.54	100	–	–
4	DMAO	60°C	trace	–	–	–	–	–
5	DEAO	30°C	4.7	0.56	1.51	78.7	87.5	2.11
6	DEAO	40°C	3.6	0.54	1.31	97.4	135.8	1.62
7	DEAO	50°C	2.9	0.69	1.31	96.4	118.5	1.68
8	DEAO	60°C	3.0	0.77	1.81	100	–	–
9	DEAO	70°C	0.5	0.23	1.39	100	–	–
10	DEAO	80°C	trace	–	–	–	–	–

^a General polymerization conditions: $[Fe] = 5 \times 10^{-6} M$, $[Al] = 5 \times 10^{-3} M$, $[Zn] = 1 \times 10^{-2} M$, $t = 30$ min, $P_{ethylene} = 4$ atm, solvent = 50 mL toluene.

^b In 10^6 g PE/molFe·h·atm.

^c In 10^3 g/mol, Measured by GPC.

5000 rpm for 20 s. Subsequently, the samples were annealed at 90°C for 10 h under vacuum.

Compatilizer for LLDPE/PEG Blends

To comprehend the potential of PE-*b*-PEG as compatilizer, the polymer blends LLDPE/PEG with and without PE-*b*-PEG were prepared by solution mixing in toluene under argon atmosphere. The samples were chopped into small pieces and compressed in a mold at 180°C to form a thin film. The mold was quenched in an ice-water bath and then PEG in the film was extracted with CH₂Cl₂. The final blend membranes were dried under vacuum at 50°C for 24 h. The surfaces of the blends were platinum coated and the morphology was studied by SEM.

Characterizations and Measurements

The molecular weights and molecular weight distributions of the polymers were measured by gel permeation chromatography (GPC) in a PL 220 GPC instrument (Polymer Laboratories, Church Stretton, UK) at 150°C in 1,2,4-trichlorobenzene with 0.0125% butylatedhydroxy toluene (BHT). Three PL mixed B columns (500–107) were used. Universal calibration against narrow polystyrene standards was employed.

¹H-NMR measurement of PEG-NCO was conducted on Varian-Inova-500Hz spectrometer using deuterated chloroform (CDCl₃) as solvent. The other ¹H-NMR spectra were performed on Varian Mercury 300 Plus instrument in the pulse Fourier mode and recorded with deuterated 1, 2-dichlorobenzene at 120°C.

The differential scanning calorimetry (DSC) experiments were carried out on a TA Q200 calorimeter. The samples were firstly heated to 150°C and held for 5 min to eliminate thermal history. Subsequently, the samples were cooled to 0°C at a rate of 10°C min⁻¹ and the nonisothermal crystallization DSC curves were recorded.

Small angle X-ray scattering (SAXS) experiments were performed at BL16B1 beamline in Shanghai Synchrotron Radiation

Facility (SSRF) in China. The wavelength of X-ray was 1.24 Å and the sample-to-detector distance was set as 5100 mm. Two-dimensional (2D) SAXS patterns at 120°C were recorded. The average exposure time was 300 s for each scan. Bull tendon was used as standard material for calibrating the scattering vector. The 2D SAXS patterns were converted into one-dimensional (1D) SAXS profiles using Fit2D software.

The morphology of membrane sample was observed by FEI SIRION field emission scanning electron microscope (FESEM). The surfaces of porous membrane samples were coated with gold prior to examination.

The surface hydrophilicity of membrane was characterized by water contact angle measurement. The water droplet (volume = 1.0 μL) permeation process was recorded using speed optimum video measuring technology equipped with Dataphysics OCA20, Germany. The measurements were performed at 25°C and 60% relative humidity.

X-ray photoelectron spectroscopy (XPS, PHI 5000C ESCA system, PHI, USA) was used to investigate the chemical compositions of sample surface. Al Kα radiation (1486.6 eV) was used as photon source and run at a power of 250 W (14.0 kV, 93.9 eV) with an electron take off angle of 90° relative to the sample plane.

RESULTS AND DISCUSSION

Synthesis and Structure of PE-OH

Although MAO is the most common cocatalyst for late transition metal catalyst,⁴¹ at temperature higher than 50°C the polymerization activity dropped significantly. However, since the relatively bulky groups in ethylaluminumoxane (EAO) chains are in favor of the formation of loose iron pairs,⁴² and those loose ionic pairs simultaneously prevent an undesirable reaction between active species and aluminumoxane so it may have the potential to improve the stabilization ability of active species at

Table II. Polymerization Results and the Number of Active Centers^a

Entry	Cocatalyst	Temp. (°C)	Activity (10 ⁶ g PE/molFe·h·atm)	Sulfur content (ppm)	[C*]/[Fe]
1	DMAO	50	5.2	414	11.1
2	DEAO	50	8.1	867	36.8
3	DMAO	60	1.8	92	0.85
4	DEAO	60	4.8	223	5.60

^aGeneral polymerization conditions: [Fe] = 5 × 10⁻⁶ M, [Al] = 5 × 10⁻³ M, t = 10 min, P_{ethylene} = 1 atm, solvent = 50 mL toluene.

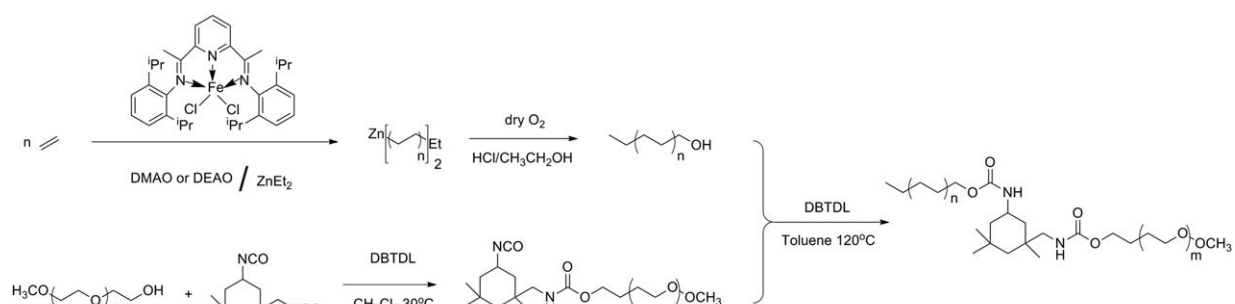
high temperature. In this part we compared the different of MAO and EAO in polymerization.

Ethylene polymerization was conducted in the presence of a bis(imino)pyridine iron complex activated with dry methylaluminoxane (DMAO) or dry ethylaluminoxane (DEAO) and ZnEt₂ at various temperatures. The results are summarized in Table I. At elevated polymerization temperature, polyethylene (PE) can be better dissolved in the solvent. According to the CCTP mechanism, the chain transfer reaction can be more efficient and last for a longer time. As a result, the polymerization activity can be enhanced and PEs with relatively higher molecular weight can be obtained. Using DMAO as cocatalyst, the polymerization activity dramatically decreased as polymerization temperature increased. At 60°C there was almost no polymer formed. This was presumably due to the decomposition of catalyst and decrease in solubility of ethylene in toluene. Interestingly, using DEAO as cocatalyst, at 30–40°C the polymerization activity was relatively lower than that using DMAO as cocatalyst. However, as the temperature further increased, the activity of DEAO-activated polymerization only slightly decreased. Even at 70°C, the polymerization activity was still satisfied. That was probably because of the active species activated by DEAO was more stable than those activated by DMAO.

In our previous works, we developed an efficient method for counting active centers in propylene or ethylene polymerization with Ziegler–Natta catalysts using 2-thiophenecarbonylchloride (TPCC) as a quenching agent.⁴⁰ It is the first time that this method was introduced to determine the number of active centers in ethylene polymerization with bis(imino)pyridine iron complex. Thus the influence of polymerization temperature and the type of cocatalyst on the number of active centers was investigated and summarized in Table II. Interestingly, the ratio

between the number of active centers and the total number of iron atoms ([C*]/[Fe]) was much higher than 1 under some conditions. In the presence of a high amount of cocatalyst for the iron systems, the chain transfer to aluminum reaction is a viable route for the formation of low molecular weight materials early in the polymerization.³⁴ Thus TPCC can not only react with Fe-terminated polymers originated from the “real” active species but also Al-terminated polymers to form 2-thiophenecarbonyl-terminated polymers. So the obtained total sulfur content coming from 2-thiophenecarbonyl groups was much higher than that originated from Fe-terminated polymers. However, one can image that the chain transfer to aluminum reaction is proportional to the number of the “real” active centers. Therefore, the values of [C*]/[Fe] should be called as the “apparent” active center concentration. At 50°C the value of [C*]/[Fe] using DEAO as cocatalyst was 3.3 times that using DMAO as cocatalyst. At 60°C the values of [C*]/[Fe] dropped significantly. The value of [C*]/[Fe] using DMAO as cocatalyst was lower than 1. As a result, the polymerization activity was very low. However, the value of [C*]/[Fe] using DEAO as cocatalyst was still as high as 5.60, resulting in moderate polymerization activity. This difference maybe caused by steric hindrance effect of methyl group and ethyl group. The bulky groups in alumoxane chains are in favor of the formation of loose iron pairs. And loose ionic pairs simultaneously prevent an undesirable reaction between active species and aluminoxane which can improve the stabilization ability of active species at high temperature.⁴²

As shown in Table I, at 30°C and 40°C the obtained PEs were bimodal regardless of the type of cocatalyst. However, at temperature ≥50°C the obtained PEs were unimodal and had higher molecular weight. Namely, at elevated temperature



Scheme 1. Synthesis of PE-*b*-PEG by a combination of CCTP and a coupling reaction of isocyanate.

Table III. Results of PE-OHs Synthesized via CCTP and PE-*b*-PEGs Synthesized via a Subsequent Coupling Reaction

Entry	Polymers	M_n , NMR	M_n , GPC	PDI	Content of PE-OH ^b	Content of PE- <i>b</i> -PEG ^c
1	PE-OH-1	1100 ^a	630	1.31	66	–
2	PE-OH-2	1300 ^a	660	1.34	62	–
3	PE-OH-3	1600 ^a	720	1.41	63	–
4	PE- <i>b</i> -PEG-1	3300 ^d	700	1.54	–	60
5	PE- <i>b</i> -PEG-2	3500 ^d	770	1.53	–	60
6	PE- <i>b</i> -PEG-3	3900 ^d	900	1.57	–	62

^a M_n , NMR were calculated by the formula: M_n , NMR = $14 \times A(b)/[A(a)/2 + A(c)/3]$. A(a), A(b), and A(c) were the area of peak (a), peak (b), and peak (c) in Figure 1, respectively.

^bIn molar percentage, calculated by the formula: Content of PE-OH = $A(a)/[A(a)/2 + A(c)/3]$. A(a) and A(c) were the area of peak (a) and peak (c) in Fig. 1 respectively.

^cIn molar percentage, calculated by the formula: Content of PE-*b*-PEG = $[44/28 \times A(a)/M_n$, PEG]/[A(b)/M_n, PE-OH]. A(a) and A(b) were the area of peak (a) and peak (b) in Figure 5, respectively, and M_n , PE-OH was in Table II.

^d M_n , NMR were calculated by the combination of the molecular weight of PE-OH, IPDI, and PEG.

uniform PEs with relatively higher molecular weight could be obtained. However, at temperature $\geq 70^\circ\text{C}$ the molecular weight dropped significantly due to the prevailing chain transfer reaction or there was almost no polymer formed.

Synthesis and Structure of PE-*b*-PEG Diblock Copolymers

The procedure to achieve PE-*b*-PEG diblock copolymer via a combination of CCTP and a coupling reaction of isocyanate is shown in Scheme 1.

The bis(imino)pyridineiron/DEAO/ZnEt₂ catalyst system allowed to prepare low polydispersity index PE-OHs with different molecular weight by CCTP at different temperature. After conducting the CCTP at 40°C for 10 min, 50°C for 30 min, or 60°C for 30 min, the resulting di(polyethylenyl)zines were oxidized, hydrolysis and extraction to obtain PE-OHs and called as PE-OH-1, PE-OH-2, and PE-OH-3, respectively (as shown in Table III). The molecular weight distribution of these PE-OHs

was narrow. Figure 1 shows the ¹H-NMR spectra of these PE-OHs. The peaks at 0.9–1.1 ppm correspond to –CH₃ of PE. The peaks at 1.2–1.9 ppm correspond to –CH₂– on PE backbone. The peaks at 3.1–3.5 ppm corresponding to –CH₂–OH, indicate the existence of hydroxyl groups at the terminal of PE. According to the ¹H-NMR spectra, the chain end functionality of the PE-OHs was about 65%.

PEG-NCO was synthesized through the condensation reaction of monomethylpoly(ethylene glycol) (PEG) with isophoronediiisocyanate (IPDI) according to the literature procedure.^{43–45} The ¹H-NMR spectra of PEG-NCOs were shown in Figure 2. The sharp peaks centered at 3.65 ppm and 3.38 ppm can be attributed to methylene protons of –CH₂CH₂O– and –OCH₃ end groups in monomer PEG respectively. The very weak peak at 4.20 ppm is attributed to methylene protons of –CH₂–OCO– in PEG end that linked with IPDI. The complex peaks centered at 1 ppm are attributed to the –CH₃ end group and –CH₂– in

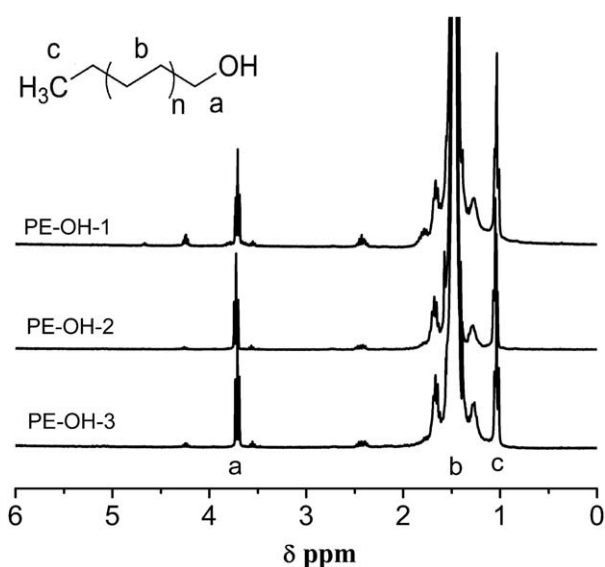


Figure 1. ¹H-NMR spectra of PE-OHs after extraction by *n*-heptane in 1,2-Dichlorobenzene-*d*₄.

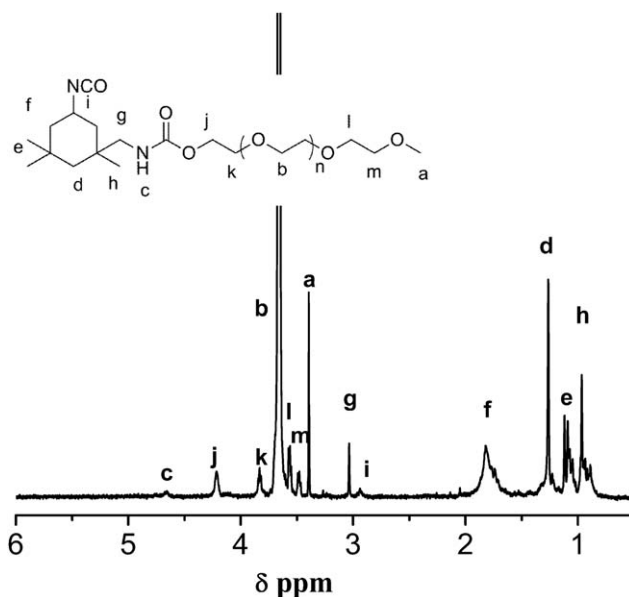


Figure 2. ¹H-NMR spectrum of PEG-NCO in CDCl₃.

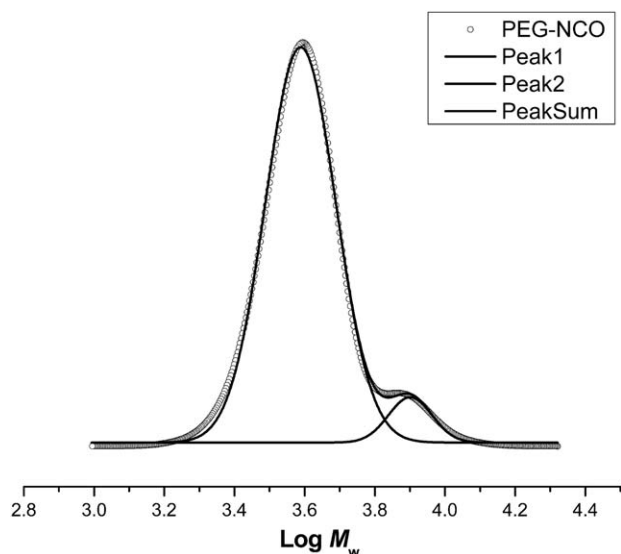


Figure 3. GPC trace of PEG-NCO.

IPDI, respectively. As shown in Figure 3, there was only a small shoulder corresponding to PEG-NCO-PEG in the GPC trace of the products. It could be estimated that about 94% of PEG was converted into the desired product.

Subsequently, PE-*b*-PEG diblock polymers were successfully synthesized by a coupling reaction of PE-OH and PEG-NCO. Their properties were listed in Table III. As shown in Figure 4 and Table II, after coupling reaction the molecular weights obviously increased and the molecular weight distributions were still narrow, indicating the successful formation of PE-*b*-PEG diblock copolymers. Figure 5 shows the ¹H-NMR spectra of PE-*b*-PEGs. The peaks at 1.1–1.25 ppm correspond to –CH₂– on PE backbone. The peaks at 3.4–3.5 ppm correspond to –CH₂–O– on PEG backbone. Because this reaction is a cou-

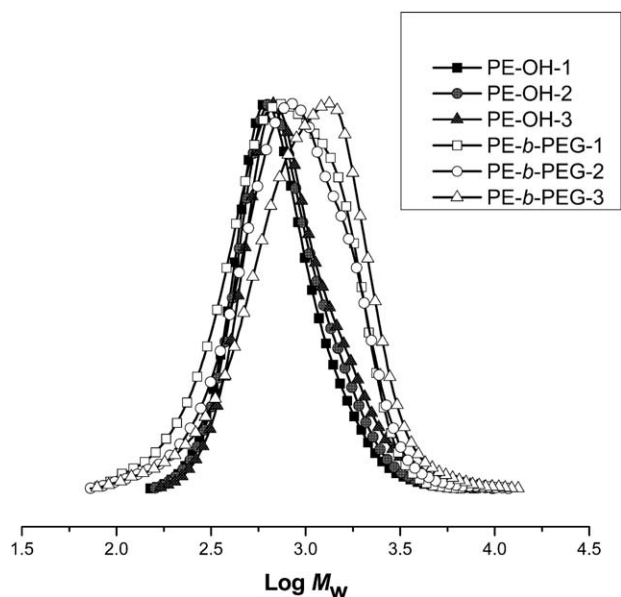


Figure 4. GPC traces of PE-OHs after extraction by *n*-heptane and PE-*b*-PEGs after extraction by acetone.

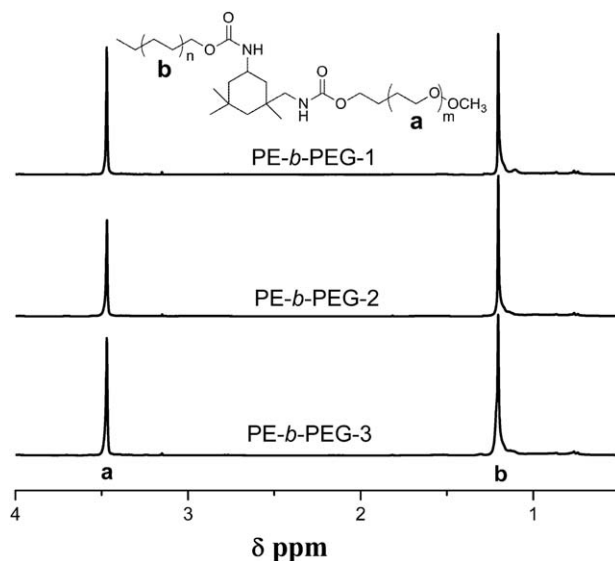


Figure 5. ¹H-NMR spectra of PE-*b*-PEGs after extraction by acetone in 1,2-dichlorobenzene-*d*₄.

pling reaction means that the molecular weight of two segments will not change, the molecular weight of two segments we can use the data of raw materials. And with the data in ¹H-NMR spectra we can calculate the molar content of the diblock copolymer with the formula in Table III. The results were also listed in Table III. Compared with the content of PE-OH that we can calculate that the conversions of these reactions were more than 90%, namely, this method is high efficient and high conversion.

Thermal Characterization of PE-*b*-PEG Diblock Copolymers

Figure 6 shows the DSC cooling scans of the diblock copolymers. All the DSC scans of copolymers display two crystallization exotherms. That means the both blocks of PE-*b*-PEG diblock copolymers are able to crystallize when cooling down from the melt state. The peaks at about 15°C correspond to the crystallization of PEG block and the peaks at about 95°C correspond to de crystallization of PE block.

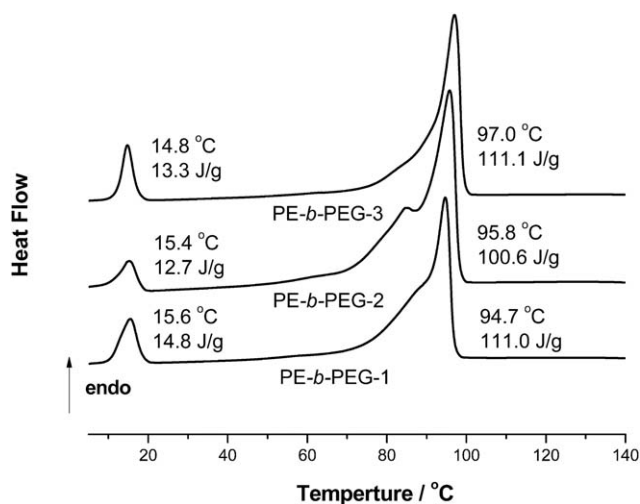


Figure 6. DSC curves of PE-*b*-PEGs at a cooling rate of 10°C/min.

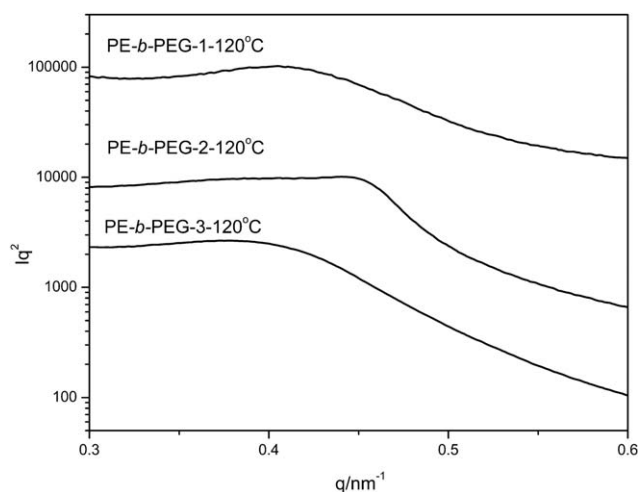


Figure 7. SAXS patterns at 120°C of PE-*b*-PEG diblock copolymers.

Also we can see that, as the molecular weight of PE block increased, the T_m of PEG block decreased slightly, on the contrary, the T_m of PE block increased slightly.

Morphological Characterization of PE-*b*-PEG Diblock Copolymers

Polyethylene-*b*-poly (ethylene oxide) (PE-*b*-PEO) copolymer as double crystalline it was observed that the phase morphology changes from lamellar to perforated lamellar, to gyroidal, to cylindrical, and to spherical while change the temperature.^{46–48} The segregation strength is governed by the product χN , where χ is the Flory–Huggins interaction parameter and N is the number of segments per chain. When χN is very small, micro-phase separation is driven by the free energy of crystallization and inducing a disordered phase.^{49,50} The values of segregation strength for copolymers was calculated and the results were 3.0 for PE-*b*-PEG-1, 3.3 for PE-*b*-PEG-2, and 3.7 for PE-*b*-PEG-3 respectively, where the values of the solubility parameters (δ) were calculated by Van Krevelen's group contribution theory.⁵¹ The product χN dictates the degree to which the A and B blocks segregate. All the copolymers were characterised by

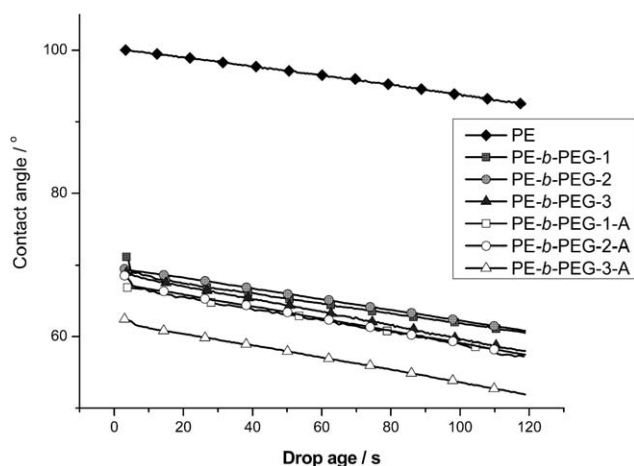


Figure 8. Membrane hydrophilicity properties of PE membrane modified with PE-*b*-PEG as surface modification agent.

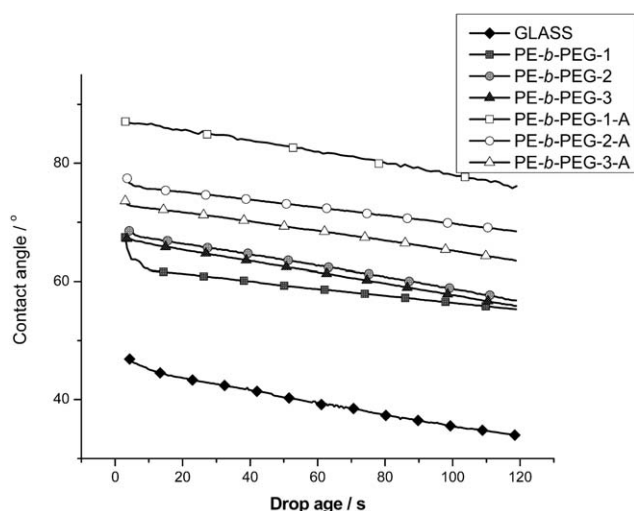


Figure 9. Membrane hydrophilicity properties of glass sheet modified with PE-*b*-PEG as surface modification agent.

SAXS. The measurements were performed at 120°C to investigate the mesophases structure. In the SAXS results (Figure 7), for all the samples no reflection were observed at test temperature. This suggests that the copolymers not featured a heterogeneous phase structure and the chains were completely disordered. As shown in Table III, in the product of coupling reaction there was about 40 mol % of polyethylene without terminal –OH groups remained. This part of polyethylene could not be separated easily from PE-*b*-PEG diblock copolymers. The existence of this part of polyethylene could affect the mesophases and the crystal structure of PE-*b*-PEG diblock copolymers. Hence, PE-*b*-PEG diblock copolymers prepared in this article is unsuitable for studying on the phase morphology changes.

The Application of PE-*b*-PEG Diblock Copolymers

Surface Modification Agent. Commonly, surface coating is the simplest strategies to endow hydrophobic membranes with hydrophilic properties.

Water contact angle (CA) measurement is a regular method to characterize the surface relative hydrophobicity and wettability characteristics. As shown in Figure 8, the initial CA of original PE membrane was as high as 100.2°. After being modified by PE-*b*-PEGs, the initial CA remarkably decreased to about 68.0°. It seemed that the chain length of PE segment did not affect CA much. However, after being annealed, the initial CA of modified PE membranes decreased gently with the increase in chain length of PE segment. Especially, in the case of sample PE-*b*-PEG-3-A, the initial CA was only 62.4°. 120 s later, the value of CA was as low as 52.1°. It indicated that during the period of annealing more PE-*b*-PEGs assembled orderly on the surface of LLDPE membrane which gave rise to more PEG segments in the interface between PE-*b*-PEG and air. The longer the PE segments were the more PEG segments enriched on the surface. The surface composition of sample PE-*b*-PEG-3 was characterized by XPS analysis to verify our explanation and the results were shown in Figure 10. There were two emission peaks can be observed at 283 eV for C_{1s} and at 531 eV for O_{1s} ,

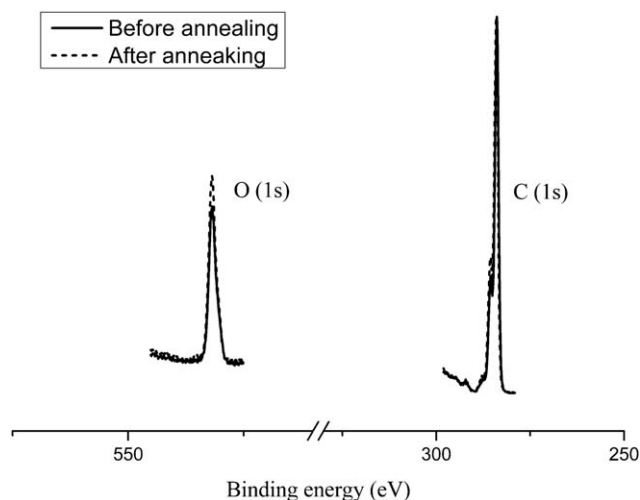


Figure 10. Survey XPS spectra of PE membrane modified with PE-*b*-PEG-3 as surface modification agent.

respectively. The simultaneous increase of the intensity of O_{1s} peak after annealing and the O/C atomic ratio was increased from 0.18 to 0.22, that means the PEG segments was enriched on the surface.

As shown in Figure 9, the initial CA of original glass sheet was 47.0° . After being modified by PE-*b*-PEGs, the initial CA increased to about 68.0° . Similarly, the chain length of PE segment did not affect CA much. However, after being annealed, the initial CA of modified PE membranes increased gradually with the decrease in chain length of PE segment. Especially, in the case of sample PE-*b*-PEG-1-A, the initial CA was as high as 87.1° . 120 s later, the value of CA was still higher than 75.8° . Obviously, the annealing treatment made more PE-*b*-PEGs assembled orderly on the surface of glass sheet which gave rise to more PE segments in the interface between PE-*b*-PEG and air. The shorter the PE segments was, the more PE segments enriched on the surface. The surface composition of sample PE-*b*-PEG-1 was also characterized by XPS analysis and the results were shown in Figure 11. The simultaneous decrease of the

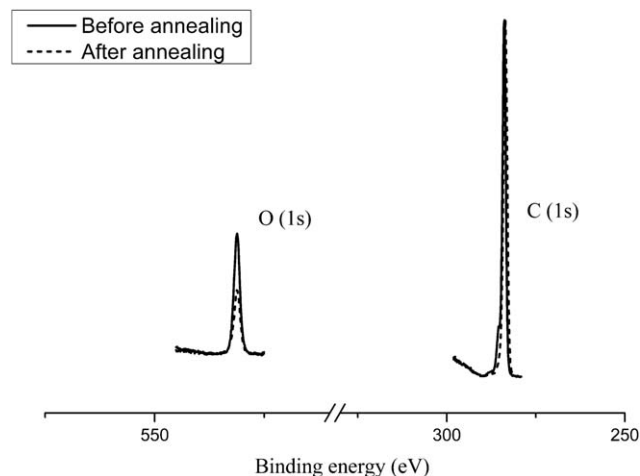


Figure 11. Survey XPS spectra of glass sheet modified with PE-*b*-PEG-1 as surface modification agent.

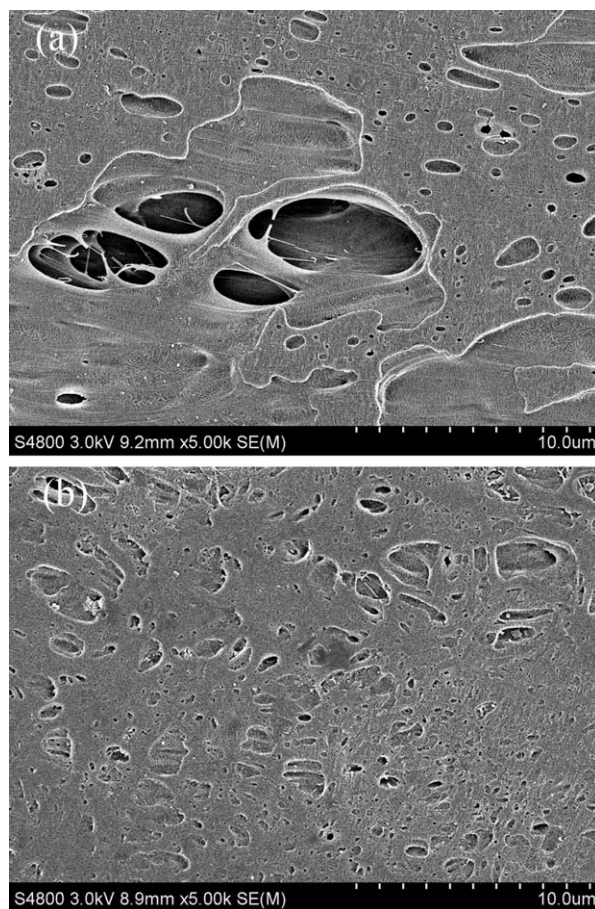


Figure 12. SEM images of polymer blends: (a) binary blends with LLDPE/PEG = 60/40 after extraction with CH_2Cl_2 ; (b) ternary blends with LLDPE/PEG/PE-*b*-PEG-3 = 60/40/5 after extraction with CH_2Cl_2 .

intensity of O_{1s} peak after annealing and the O/C atomic ratio was increased from 0.23 to 0.16, which means the PE segments was enriched on the surface.

In a word, PE-*b*-PEG is an excellent surface modification agent. It can efficiently turn a hydrophobic surface into a hydrophilic surface, or vice versa.

Compatilizer for LLDPE/PEG Blends. Figure 12 shows the surface morphology of LLDPE/PEG (LLDPE/PEG = 60/40, weight ratio) and LLDPE/PEG/PE-*b*-PEG (LLDPE/PEG/PE-*b*-PEG-3 = 60/40/5, weight ratio) blends. PE-*b*-PEG-3 was chosen as compatilizer because of the longest PE segment in it, which was theoretically compatible with LLDPE the best. In Figure 10(a), since PEG was extracted and removed by CH_2Cl_2 , many large spherical and hemispherical holes could be observed in LLDPE/PEG blend. This “ball and socket” morphology obviously representing that some PEG domains were pulled out of the LLDPE matrix because of the poor compatibility between LLDPE and PEG. But for ternary blends containing PE-*b*-PEG-3 as the compatilizer [as shown in Figure 10(b)], those holes dispersed in the LLDPE matrix were much smaller and more uniform than that in LLDPE/PEG blend. This indicated that PE-*b*-PEG could efficiently improve the interfacial adhesion between PE

and PEG. Namely, PE-*b*-PEG is an effective compatilizer for polar polymers and nonpolar polymers.

CONCLUSIONS

In conclusion, PE-OHs with high molecular weight can be prepared by CCTP using ethylene as monomer with 2,6-bis[1-(2,6-diisopropylphenyl)imino ethyl] pyridine iron (II) dichloride/DEAO/ZnEt₂ at temperature $\geq 60^{\circ}\text{C}$ and subsequent *in situ* oxidation with oxygen. Compared with DMAO, using DEAO as cocatalyst the active centers of the catalyst system were more stable. PEG-NCO can be conveniently synthesized through the condensation reaction of PEG with IPDI. Then PE-*b*-PEGs can be efficiently and economically synthesized by a coupling reaction of PE-OH and PEG-NCO. DSC results show that the both blocks of PE-*b*-PEG diblock copolymers are able to crystallize and the SAXS results suggested that the copolymers were completely disordered at melt state. These diblock copolymers were excellent surface modification agents. They can efficiently turn a hydrophobic surface into a hydrophilic surface, or vice versa. Meanwhile, the diblock copolymer was an effective compatilizer for polar polymers and nonpolar polymers.

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