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ORIGINAL PAPER

Well-defined PE-*b*-PTFE diblock copolymers via combination of coordination chain transfer polymerization and condensation reaction: Facile preparation and surface modification of polyethylene film

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ABSTRACT

In this paper, a series of well-defined polyethylene-b-polytetrafluoroethylene diblock copolymers (PE–*b*–PTFEs) were prepared by a coupling reaction of hydroxyl-terminated polyethylene (PE–OH) and isocyanate-terminated 1H,1H-perfluoro-1-tetradecanol (PFDO–NCO). PE–OH was prepared by the coordination chain transfer polymerization using 2,6-bis[1-(2,6-diisopropylphenyl)imino ethyl] pyridine iron (II) dichloride /dry ethylaluminoxane/ZnEt$_2$ as catalyst and subsequent in situ oxidation with oxygen. PFDO–NCO was synthesized through the condensation reaction of 1H,1H- perfluoro-1-tetradecanol (PFDO) with isophoronediisocyanate (IPDI). Subsequently, the thermal characterization and the application of these diblock copolymers were investigated. The relationship between the molecular structure and the properties was disclosed. The results indicated that the diblock copolymers were effective surface modification agents for linear low density polyethylene (LLDPE). After that the PE–*b*–PTFE being spin-coated onto the surface of LLDPE film, the film was dramatically turned into a superhydrophobic film with a water contact angle as high as 151.4º. This kind of film is potential to be used as self-cleaning, anti-icing and anticorrosion material. **Polyolefins J (2017) 4: 191-200**

Keywords: Polyethylene; polytetrafluoroethylene; diblock copolymer; synthesis; application.

INTRODUCTION

The structure and chemical composition of the outermost surface layer govern the surface properties of materials. Fluorinated polymers are widely used as surface modification agents to reduce the surface energy of materials due to their extremely low surface energy. In addition, the incorporation of fluorine atoms into the polymer structure results in other peculiar properties such as low refractive index, low friction coefficient and chemical resistance [1]. Water and oil repellents for textiles, surface protector of stone and polymer films, mold releasing agent, molecular lubricant, bio-fouling release coating and so on, represent the typical applications of fluorinated polymers as surface modification agents [2-8]. With very special properties, fluoropolymers have potential for a wider range of applications, but their uses are limited by poor adhesion properties.

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The poor adhesion is especially problematic when one attempts to put fluoropolymer film as a functional layer onto the surface of other materials.

As the most voluminous and widely used commodity polymers, polyolefins have become the indispensable materials to our society with a worldwide production exceeding 100 million tons per year. Polyethylene (PE) is deemed as one of the most useful polyolefins for its durability, ductility, toughness, corrosion resistance and broad use temperature (T_m = 130°C; Tg < 100°C). However, polyolefins' inherent shortcomings, for example poor adhesion and incompatibility with other materials due to their nonpolar character impede their application in many areas, where more expensive and less environmentally friendly materials are used. Extensive efforts have been made to develop modified polyolefins that contain polar groups. Such materials can possess both improved surface and bulk properties, such as barrier properties, toughness, adhesion, printability, wettability, miscibility with other polar polymers and so on.

Polytetrafluoroethylene (PTFE) has extremely low dielectric constant and remains stable over a wide range of temperature, humidity and electromagnetic frequency. It has many desirable properties, such as chemical resistance, electrical stability, low coefficient of friction and mechanical stability at −260 ~ 260°C under continuous operations [9]. While in industry, PTFE is commonly used when in need of high frequency materials, its favorable properties have led many other applications such as non-stick coating for pans and other cookwares, solid lubricant, cable insulation or printed circuit boards used under microwave frequencies. Another well-known property of PTFE is that it possesses low surface energy and low friction coefficient, and in most of the cases it has a very low adhesiveness to different materials [10].

Although PE and PTFE are incompatible [11], scientists are keen to seek out methods to blend them together for new materials with special properties and a wide range of uses. For example, Ishida [12] tried to mixed PE and PTFE together by mechanical alloying treatment. He demonstrated that the miscibility of PE and PTFE began to occur after a period of high-energy vibration ball-milling. Uyama et al. [13] provided a series of bio-adaptable 2-layer PTFE/PE

laminated sheets by a new adhesion method, a double-step treatment consisting of applying low dose (≤0.43 MGy) homogeneous low energy electron beam irradiation (HLEBI) to the 2-layer assembly where the HLEBI penetrates through the PTFE and PE layers, respectively, prior to hot-press under 5 MPa at 433K. Although, adhesion of the PTFE/PE sheets could not be observed without the new double-step treatment, bonding forces were created as evidenced by the mean adhesive forces of peeling resistance (°FP). The adhesion could not be observed without HLEBI. On the other hand, application of a small dose of HLEBI (less than 0.43 MGy) prior to hot-press lamination enhanced the °FP at each PP (peeling probability). The maximum °FP values at each PP (0.06, 0.50 and 0.94) of the laminated sheet irradiated at 0.13, 0.13 and 0.22 MGy were 5.44, 10.7 and 19.7 Nm^{-1}, respectively. Block copolymers typically undergo microphase separation, adopting composition-dependent morphologies that comprise domains with nanoscopic dimensions. Block copolymers embody the physical attributes of each constituent combined with unique properties derived specially from the microphase separation. Thompson et al. [14] polymerized 1,3-butadiene with living anionic polymerization using sec-butyllithium as an initiator and hexane as the solvent. The living polybutadiene chains were capped with diphenylethylene before termination with a multi-C_8F_{17}-fluorocarbon-functionalized aryl ether bromide group. The fluorocarbon end-capped polybutadiene was saturated with hydrogen at 500 psi in the presence of a Pd catalyst. Thus a series of diblock copolymers containing PE segments and PTFE segments were prepared and then blended with PE matrices. It was found that the surface hydrophobicity and lipophobicity were enhanced. Water contact angles of >112° were observed on spin-cast blended film surfaces containing less than 1% fluorocarbon in the bulk.

In this paper, we provide a simple but high-efficient method for preparation of well-defined PE–b–PTFE diblock copolymers via the combination of coordination chain transfer polymerization (CCTP) [15, 16] and condensation reaction. Subsequently, these diblock copolymers were used as surface modification agent for linear low-density polyethylene (LLDPE). Water contact angles of >150° have been observed and

the influence of chain structure of PE–*b*–PTFE on the surface properties was systematically investigated. The synthetic route presented in this work is more facile and economical for industrial applications as compared with the literature methods.

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. 1H,1H-perfluoro-1-tetradecanol (96%) was purchased from J&K Scientific Ltd., China and heated at 120ºC for 2 h under vacuum to remove H_2O. Di-n-butylamine (99.5%), dibutyltindilaurate (DBTDL), isophoron diisocyanate (IPDI) and bromocresol green (+95%) were purchased from J&K Scientific Ltd., China and used as received. KMnO$_4$ (≥99.5%), anhydrous ethyl ether, anhydrous tetrahydrofuran (THF) were purchased from Sinopharm Chemical Reagent Co., Ltd., China and used as received. 2,6-Bis[1-(2,6-diisopropylphenyl)imino ethyl] pyridine iron (II) dichloride was synthesized according to the literature procedure [17]. Ethylaluminoxane (EAO) was prepared according to a previously reported method [18-21]. Dried ethylaluminoxane (DEAO) was prepared according to the literature procedure and then diluted by toluene to 1.0 M [20]. LLDPE ($M_n = 1.05 \times 10^5$, $M_w/M_n = 4.8$, [1-hexene] = 3.6 mol%) was prepared by our laboratory with a fourth-generation Ziegler-Natta catalyst.

0.1 g bromocresol green was dissolved into 100.0 mL ethanol/deionized water (volume ratio = 20 : 80) mixture to provide bromocresol green indicator. 2.6 g di-n-butylamine was dissolved into appropriate amount of acetone. The solution was transferred into a 200 mL volumetric flask. Acetone was added to the calibration mark. The di-n-butylamine/acetone solution was kept in dark place or prepared just before use.

Synthesis of hydroxyl-terminated polyethylene (PE–OH)

The synthesis of PE–OH via CCTP followed a similar procedure to that previously reported in the literature [22]. A 2,6-bis[1-(2,6-diisopropylphenyl)imino ethyl] pyridine iron (II) dichloride / 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 or 0.7 MPa. The polymerization temperature was maintained at 40ºC, 60ºC or 80ºC. After 30 min of polymerization, the product was oxidized in-situ by introducing oxygen flow at 100ºC for 2 h. The resulting mixture was poured into acidic ethanol. The white powder was filtered, washed with plenty of ethanol and dried under vacuum at 60ºC. The product obtained at 0.4 MPa ethylene and ≤ 60ºC was extracted by n-heptane to remove the high molecular weight PE without –OH group (the active species forming high molecular weight PE cannot react with ZnEt$_2$ efficiently) and then dried under vacuum at 60ºC to give relatively pure PE–OH.

Synthesis of isocyanate-terminated 1H,1H-perfluoro-1-tetradecanol (PFDO–NCO)

3.5 g (5 mmol) dry 1H,1H-perfluoro-1-tetradecanol (PFDO, M_n= 700 g/mol) and 35 mL anhydrous THF were mixed together in a 100 mL Schlenk flask. 11.1 g (50 mmol) IPDI was charged into another 100 mL Schlenk flask under N$_2$ atmosphere and 2~3 drops of DBTDL was added into the flask as a catalyst. After IPDI being heated to 30ºC, the PFDO/THF mixture was introduced dropwise via cannula and stirred for 3 h. The product was isolated by the dissolution-precipitation technique with CHCl$_3$ as solvent and anhydrous ethyl ether as precipitant. This procedure was repeated at least twice. The obtained white powder was filtered and dried under vacuum at 40ºC for 24 h to give 4.23 g of PFDO–NCO.

The percentage of PFDO–NCO in the obtained product was determined by 'di-n-Butylamine-Acetone' method [23]. Firstly, –NCO groups reacted with excess di-n-butylamine. The unreacted di-n-butylamine was then determined by back titration with standard

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HCl solution. According to Eqs. 1-3, the percentage of PFDO–NCO in the obtained product could be calculated:

$$n_{PFDO-NCO} = (V_0 - V) \times c / 1000 \quad (1)$$

$$n_{2PFDO} = \frac{m - (M_{PFDO-NCO} \times n_{PFDO-NCO})}{M_{2PFDO}} \quad (2)$$

$$n_{NCO} = \frac{n_{PFDO-NCO}}{n_{PFDO-NCO} + n_{2PFDO}} \quad (3)$$

where V_0 (mL) is the volume of standard HCl solution consumed by blank sample, V (mL) is the volume of standard HCl solution consumed by the unreacted di-n-butylamine remained in the testing sample, c (mol/L) is the molar concentration of standard HCl solution, m (g) is the quantity of testing sample, MPFDO-NCO is the molecular weight of PFDO–NCO and nPFDO-NCO is the mole of PFDO–NCO. Since two PFDOs could be coupled by one IPDI via the reaction between –NCO and –OH, there was some PFDO–IPDI–PFDO (as shown in Scheme 1) produced as a byproduct. M_{2PFDO} is the molecular weight of PFDO–IPDI–PFDO and n_2PFDO is the mole of PFDO–IPDI–PFDO.

1.0 g sample was put into a dry iodine flask. 10.0 mL acetone was added to dissolve the sample. After the sample being dissolved completely, 20.0 mL di-n-butylamine/acetone solution was added. The lid was covered and the flask was shaken vigorously and left to rest for 15 min. Subsequently, 3 drops of bromocresol green indicator was added and the standard HCl solution (0.1 M) was used as titrant till the end point was approached (the color of the solution turned from blue to yellow). The titration was performed triplicate. Meanwhile, a blank experiment was carried out.

Surface modification of LLDPE and annealing treatment

The LLDPE film was washed by n-hexane, ethanol, and deionized water for three times respectively and then dried in vacuum at 60ºC for 8 h. Designated amount of PE–b–PTFE diblock copolymer was dissolved in 10 mL toluene (1 wt %). The solution was poured onto the LLDPE substrate at 100ºC. Then the substrate was spun at 5000 rpm for 20 s. Subsequently, the samples were dried by airing.

The test films (pristine and modified LLDPE films) were put into a sealed stainless steel container. Then the container was connected to a vacuum line and immersed into a bath containing silicone oil at 110ºC. The test films were annealed under a N₂ atmosphere with standard Schlenk techniques for 10 h.

Characterizations and measurements

Molecular weight and molecular weight distributions of polymers were measured by gel permeation chromatography (GPC) in a PL 220 GPC instrument (Polymer Laboratories, Church Stretton, UK) at 150ºC in 1,2,4-trichlorobenzene with 0.0125% butylated hydroxy toluene (BHT). Three PL mixed B columns ($500 \sim 1 \times 10^7$) were used. Universal calibration against narrow polystyrene standards was employed.

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

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

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

FTIR-ATR spectroscopy was carried out on a Bruker Vector 22 FTIR spectrophotometer. The spectra were measured in the wave number range of 4000~500 cm⁻¹. The spectra were collected by cumulating 32 scans at a resolution of 2cm⁻¹.

RESULTS AND DISCUSSION

Synthesis and structure of PE–OH

As shown in Scheme. 1, in order to obtain PE–b–PTFE
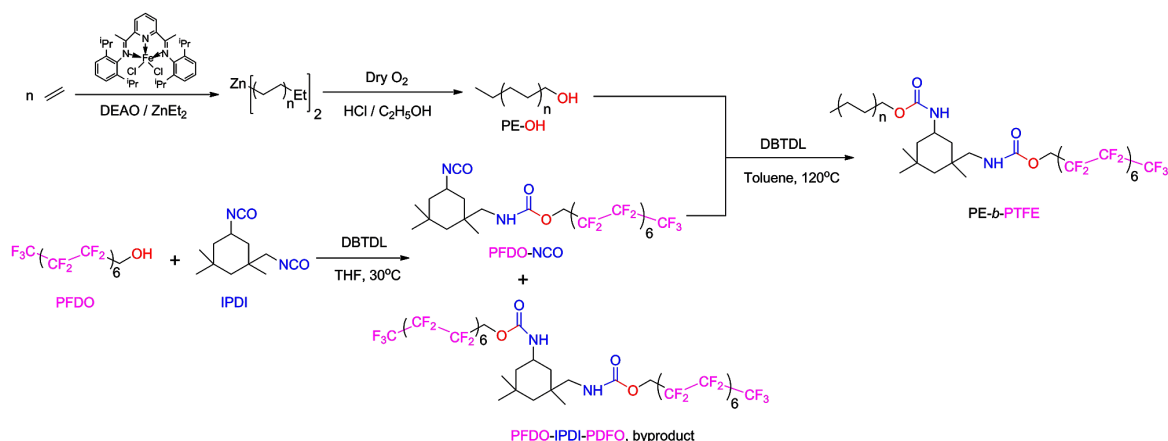
Scheme 1. Synthesis of PE–b–PTFE by combination of CCTP and coupling reaction of isocyanate.

we needed to prepare hydroxyl-terminated polyethylene (PE–OH) first. Previously we developed a more efficient catalytic system to prepare PE–OH. Using dried ethylaluminoxane (DEAO) as cocatalyst the polymerization of ethylene can be performed at elevated temperature as high as 60ºC and provide PE–OH with a satisfactory catalytic activity. This method for preparation of polyethylene segment is rather different from the saturation of polybutadiene with hydrogen gas [14]. The polymerization results and the measurement of the obtained PE–OH are summarized in Table 1.

As shown in Table 1 and Figure 2, the molecular weight distribution of these PE–OHs was rather narrow. The number average molecular weight was not higher than 3.200 kg/mol that was much lower than that of polyethylene segment (4.2 ~ 26.8 kg/mol) prepared by Thompson et al. [14]. Thus PE–b–PTFEs with relatively higher content of PTFE segment could be synthesized. In such PE–b–PTFEs the unique properties of PTFE segment could perform better. Through coordination chain transfer polymerization and subsequent in situ oxidation with O_2, 62 ~ 66 mol% of polyethylene chain ends were capped by hydroxyl groups. The rest part was polyethylene with the same molecu-

lar weight of PE segment in PE–OHs.

Synthesis and structure of PFDO–NCO

1H,1H-perfluoro-1-tetradecanol (PFDO, M_n= 700 g/mol) reacted with excessive isoporondiisocyanate to afford isocyanate-terminated ^{1}H,1H-perfluoro-1-tetradecanol (PFDO–NCO). The reaction product was characterized by 1H-NMR and shown in Figure 3. As shown in Figure 3, there was only one peak at about 1.5 ppm for PFDO. However, this peak completely disappeared in PFDO–NCO. It indicated that the reaction between PFDO and IPDI was very efficient. Furthermore, those chemical shifts on the ^{1}H-NMR spectrum of the reaction product could be precisely assigned to the proton on different positions of PFDO–NCO. Namely, the target compound PFDO–NCO was successfully prepared. By titration via 'di-n-Butylamine-Acetone' method, 94 mol% of 1H,1H-perfluoro-1-tetradecanol was capped by isocyanate groups.

Synthesis and structure of PE–b–PTFE

After PE–OHs and PFDO–NCO being prepared, PE–b–PTFEs were synthesized by coupling reaction between PE–OHs and PFDO–NCO. The obtained

Table 1. Results of PE–OHs synthesized via coordination chain transfer polymerization.

Polymers	Temp (ºC)	E_p [a] (MPa)	Act [b]	$M_{n\ NMR}$ [c]	$M_{n,\ GPC}$	PDI	Cont of PE–OH [d]
PE–OH-1100	40	0.4	7.25	1100	630	1.31	66
PE–OH-1600	60	0.4	5.05	1600	720	1.41	63
PE–OH-3200	80	0.7	2.84	3200	1690	1.55	62

[a]Ethylene pressure.
[b]Polymerization activity, in 106 g PE/mol Fe-h-atm.
[c]$M_{n,\ NMR}$ was calculated by the formula: M_n, NMR = 14 × 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.
[d]In 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 .
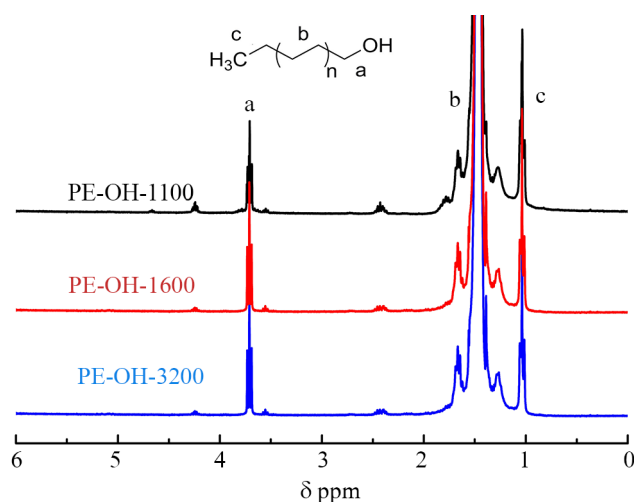
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Figure 1. ¹H-NMR spectra of PE-OHs in 1,2-dichloroben-zene-d4.

Figure 3. ¹H-NMR spectra of PFDO and PFDO–NCO in CDCl₃.

product was characterized by 1H-NMR and the results are shown in Figure 4. Compared with Figure1 (¹H-NMR spectra of PE–OH), after coupling reaction the chemical shift at about 3.7 ppm corresponding to –CH₂–OH in PE–OH completely disappeared. It indicated that almost 100% of PE–OH reacted with PFDO–NCO. Moreover, the chemical shifts at 0.5 ~ 1.0 ppm could be attributed to methylene protons (–CH₂–) and methyl protons (–CH₃) on the six-membered ring of IPDI. And the sharp peaks centered at 1.2 ppm could be attributed to methylene protons (–CH₂–) on the PE backbone. According to the ¹H-NMR spectra, the target compounds PE–*b*–PTFEs were successfully prepared.

Figure 5 shows the DSC curves of PE–b–PTFEs in heating scan. As shown in Figure 5, the melting range of PE–OH-1600 is very broad, ranging from 80ºC
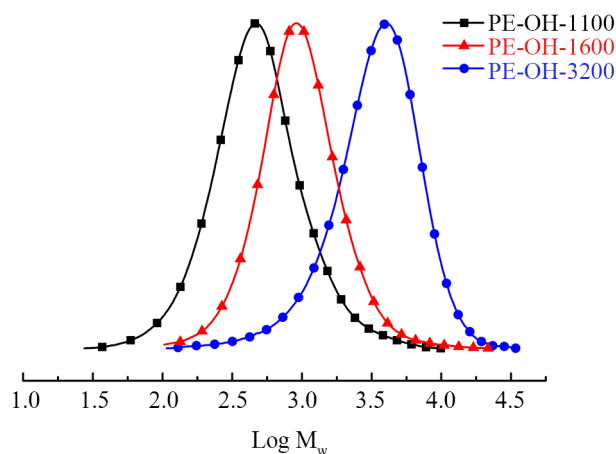
~120ºC. The introduction of PTFE segment to some extent reduced the melting range and the melting enthalpy. In the case of PE1600–*b*–PTFE700, the melting range fell into the range of 80ºC ~110ºC and the melting enthalpy dropped from 216.4 J/g to 86.7 J/g. It indirectly verified that the PE segment and PTFE segment were covalently connected, which caused strong interactions on their properties. Meanwhile, the melting range and the melting enthalpy of PE–*b*–PTFEs depended on the length of PE segment. As the length of PE segment decreased, both the melting range and the melting enthalpy of PE–*b*–PTFEs decreased. Although the existence of PTFE segment diminished the
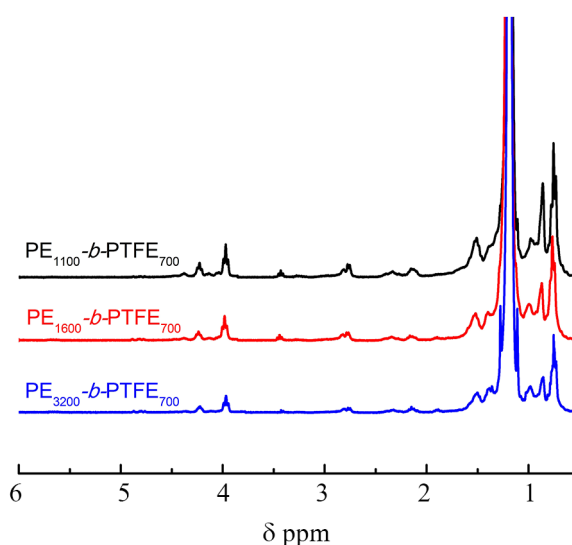

Figure 2. GPC traces of PE-OHs after extraction by n-heptane.

Figure 4. ¹H-NMR spectra of PE–b–PTFEs in 1,2-dichloro-benzene-d4.

crystallization ability of PE segment to some extent, PE segment could still crystallize well. The crystallinity degree of PE–*b*–PTFEs was higher than 29% and the melting point of PE–b–PTFEs was higher than 85ºC. This offered a possibility for PE–*b*–PTFE and linear low-density polyethylene (LLDPE) to interact with each other via co-crystallization.

Use of PE–*b*–PTFE as surface modification agent of a LLDPE substrate

An LLDPE substrate was covered by very thin layer of PE–b–PTFE via spin-coating. The water contact angles were measured and shown in figure 6. The water contact angle of the pristine LLDPE film was 100.2º. After being modified, the water contact angle of the modified LLDPE film was higher than 132.2º. As the length of PE segment decreased, the water contact angle of the modified LLDPE film increased significantly. Especially, using PE1100–*b*–PTFE700 as modification agent, the water contact angle was as high as 145.0º. Since annealing treatment can make the polymer chains rearrange orderly to some extent [24], we can expect that the PE segment and PTFE segment in PE–*b*–PTFE can undergo microphase separation more completely during the process of annealing. Thus the modified LLDPE films were annealed for 10 h under 110ºC, which was a little lower than the melting point of LLDPE. Interestingly, the water contact angles were enhanced significantly. Particularly, the water contact angle of the LLDPE film modified by PE1100–*b*–PTFE700 was as high as 151.4º, which

could be defined as a superhydrophobic surface. This kind of surface is important in many industrial and biological processes, such as prevention of the adhesion of snow to antennas and windows, self-cleaning traffic indicators, the reduction of frictional drag on ship hulls, metal refining, stain-resistant textiles and membranes, and cell motility [25-27]. Similarly, the water contact angle of the modified LLDPE film still increased as the length of PE segment decreased.

Change of chemical composition of the outermost surface layer of the modified LLDPE films and those annealed films was investigated by FTIR-ATR spectroscopy. As shown in Figure 7, the 1460 cm^{-1} band is due to $-CH_2-$ bending on the PE segment. The 1241 cm^{-1} and 1224 cm^{-1} bands are due to $-CF_2-$stretching vibration on the PTFE segment [28]. In the FTIR-ATR spectra of the LLDPE surfaces covered by PE1100–b–PTFE700, PE1600–b–PTFE700 and PE3200–*b*–PTFE700, respectively, intensity of the 1460 cm^{-1} bands were not much different among them. However, intensity of the 1241 cm^{-1} and 1224 cm^{-1} bands were rather different among them. As the length of PE segment decreased, the intensity of the 1241 cm^{-1} and 1224 cm^{-1} bands increased significantly. It indicated that the PTFE segments of PE–b–PTFE with shorter PE segment could be more efficiently enriched in the interface of PE–*b*–PTFE and air. Therefore, water contact angle of the LLDPE surface modified by PE1100–*b*–PTFE700 was the highest. After annealing treatment, the intensity of the 1241 cm^{-1} and
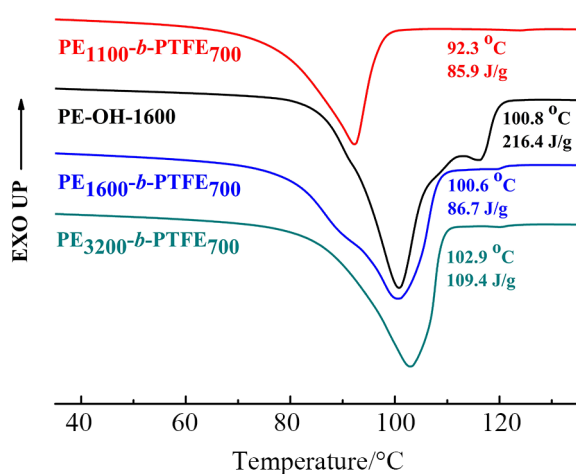

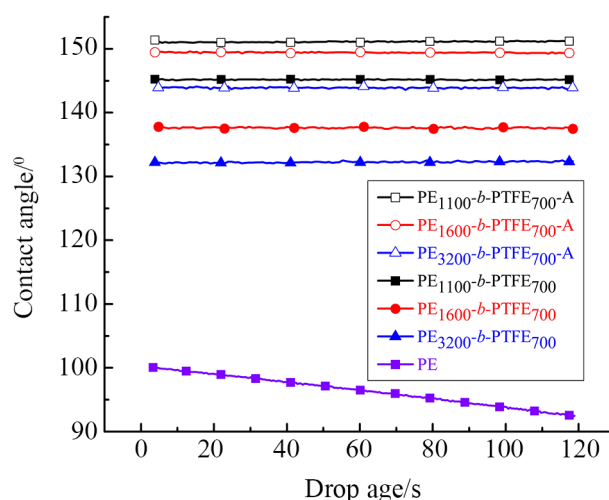**Figure 5**. DSC curves of PE–b–PTFEs at a heating rate of 10ºC /min.

Figure 6. Water contact angle measurement results. (A-terminated sample = sample with annealing treatment.)

1224 cm^{-1} bands (the dotted lines in Figure 7) did not change much. However, intensity of the 1460 cm^{-1} bands dropped obviously, especially in the case of PE1100–*b*–PTFE700. It indicated that the PTFE segment was further enriched in the interface between PE–*b*–PTFE and air and resulted in superhydrophobic surface. As stated above, the PE segment in PE–*b*–PTFE could crystallize independently. During the process of annealing treatment, LLDPE and PE–*b*–PTFE were partially melted together. The PE segment in PE–*b*–PTFE and the chain of LLDPE could entangle to each other. As the film was cooled down, cocrystal might be formed in the interface between the thin PE–*b*–PTFE layer and LLDPE film. Due to the existence of the cocrystal, PE–*b*–PTFE could be fixed on the surface of LLDPE film. Thus it is reasonable to expect that the hydrophobic property of the modified LLDPE film should be durable. It can be concluded that coating PE–*b*–PTFE layer as surface modifier is a simple and highly efficient way to reduce the surface energy of LLDPE film.

CONCLUSION

Well-defined polyethylene-b-polytetrafluoroethylene diblock copolymers (PE–*b*–PTFEs) can be simply and efficiently synthesized by coupling reaction of hydroxyl-terminated polyethylene (PE–OH) and isocyanate-terminated 1H,1H-perfluoro-1-tetradecanol (PFDO–

Figure 7. ATR-FTIR spectra of the surface modified LLDPE films before and after annealing treatment: A-terminated sample = annealing treatment sample.

NCO). PE–OHs with different molecular weights can be prepared by coordination chain transfer polymerization under different conditions. Thus, PE–*b*–PTFEs with different length of PE segment can be prepared. The PE–*b*–PTFEs were highly efficient surface modification agents for linear low density polyethylene (LLDPE) film. After spin-coating PE–*b*–PTFE layer onto the surface of LLDPE film, water contact angle of the film was significantly enhanced. As the length of PE segment in PE–*b*–PTFEs decreased, the water contact angle of the modified LLDPE film increased obviously. Annealing treatment is an effective method to further enhance the hydrophobicity of the modified LLDPE film. Particularly, the water contact angle of the LLDPE film modified by PE1100–*b*–PTFE700 was as high as 151.4º, which could be defined as a superhydrophobic surface. This kind of surface is important in many industrial and biological processes.

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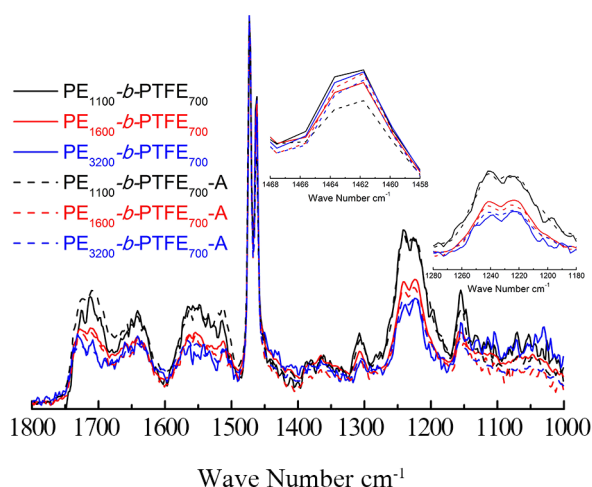
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