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# Synthesis and characterization of precisely-defined ethylene-*co*-aryl ether polymers via ADMET polymerization



<sup>a</sup> Department of Polymer Science and Engineering, Faculty of Materials Science and Chemical Engineering, Ningbo University, Ningbo 315211, China <sup>b</sup> Key Laboratory of Specialty Polymers, Grubbs Institute, Ningbo University, Ningbo 315211, China

### A R T I C L E I N F O

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### ABSTRACT

A new family of polyolefins containing various aryl ether units have been designed and synthesized, and their thermal properties were studied. We prepared six acyclic diene monomers di(undec-10-enyloxy) aryl ether by a two-step approach and the corresponding homopolymers and copolymers with 1,9-decadiene by ADMET. Subsequent hydrogenation gave the corresponding ethylene-*co*-aryl ether polymers. The structures of these polymers were confirmed by <sup>1</sup>H NMR, <sup>13</sup>C NMR and FT-IR. Additionally, crystallization behaviors and thermal properties were investigated by differential scanning calorimetry (DSC), X-ray diffraction and thermal gravimetric analysis (TGA). The results show that incorporation of these aryl ether units has improved the thermal stability of polymers. And these polymers show a tendency of semicrystallinity to amorphous state with the insertion of more rigid phenyl rings in functional sites of polymers' main chain. Interestingly, DSC analysis reveals that a sequence of melting/ crystallization phenomenon occurs in the crystalline saturated homopolymers.

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### 1. Introduction

The structure—property relationship of ethylene-based materials has attracted increasing attention. The physical and chemical properties of corresponding ethylene-based polymers can be widely modulated by manipulating the microstructural parameters, such as the nature, length and placement of the branches along the backbone. For instance, introduction of non-polar or polar functionalities via copolymerization or post-functionalization like alkyl, halogen, cyano, phenyl, hydroxyl, and carboxyl, would endow polymers with unique properties such as crystallinity, flexibility, flame retardancy, chemical resistance, impact strength, processability and adhesion [1–8]. Also, some special ethylene-based functional materials like ionomers [9,10], poly (thienylene vinylene)s (PTVs) [11], and polymer light emitting diodes (PLEDs) [12,13] received considerable attention in recent years for their potential application as electroactive materials. However, ethylene-*co*-aryl ether polymers have been rarely reported. Actually, poly (aryl ether) is a class of engineering plastics with integrated high performance such as good mechanical properties, heat resistance, and corrosion resistance, thus it has been widely used in aerospace, electronics, mechanical instruments and other fields [14,15]. Therefore it will be interesting to know if introducing the aryl ether units into the main chain of polyethylene would bring about excellent properties from both poly (aryl ether) and polyethylene.

Williamson ether synthesis [16], Claisen rearrangement [17,18] and Ullmann condensation reaction [19–21] are the general methods access to small aryl ether molecules and even polymers with only short ethylene segments incorporated. However, synthesizing ethylene-based polymers with longer ethylene segments via these methods would require long reaction time, heating and often suffer from low yields. Typical polymerization strategies for the preparation of ether incorporated polyolefins could also include transition-metal-catalyzed coordination-insertion polymerization and free radical processes, but the oxophilicity of the transition-metal polymerization catalysts which generally leads to poisoning by strong  $\sigma$ -coordination of the Lewis basic moiety of a polar vinyl monomer or poor control over branching ratios, and distribution of the polar functional groups in the polymer chain. Alternatively, ring-opening metathesis polymerization (ROMP) of functionalized





polymer

<sup>\*</sup> Corresponding authors. Department of Polymer Science and Engineering, Faculty of Materials Science and Chemical Engineering, Ningbo University, Ningbo 315211, China.

*E-mail addresses*: gongdirong@nbu.edu.cn (D. Gong), chenzhongren@nbu.edu. cn (Z.-R. Chen).

cyclooctenes [22–24] or acyclic diene metathesis (ADMET) of functionalized dienes [25–27] represents a potentially ideal method for the controlled synthesis of functional polyolefins in a single step, particularly, precisely control the identity and distribution of branches along the backbone of polyethylene, as well as functional groups incorporated in the main chain, including model copolymers of ethylene with acrylates [28], styrene [29], vinyl acetate [30], and vinyl halide [31], silicon-containing polymers [32] and chiral polymers [33] have been unprecedently achieved in the presence of Schrock' catalyst and Grubbs' series of catalysts.

The bisphenols with two hydroxyphenyl functionalities are potentially good candidates for constructing aryl ether architecture in polymer chain. In this research, we have selectively introduced 1,4-benzenediol group, 4,4'-biphenol group and other four types of bisphenol groups as co-monomers to form corresponding ethylene-co-aryl ether polymers via ADMET. The nomenclature of polymers is expressed in the following manner: "BP" stands for polymers containing bisphenols units, the digital or letter following the "BP" refers to the type of bisphenols units, subsequent "P" stands for unsaturated polymer, and "HP" refers to hydrogenated polymer, the final digital stands for serial number. For example, "BPF-HP4" refers to hydrogenated polyolefin 4 with bisphenol F (4,4'-Dihydroxydiphenylmethane). Additionally, "dd" is added to the abbreviations for copolymer with 1,9-decadiene, like BPFdd-HP8. All polymers' chemical structures have been characterized by FT-IR, <sup>1</sup>H and <sup>13</sup>C NMR techniques, and their thermal properties, crystallization behaviors were also systematically investigated by DSC. TGA and X-ray diffraction.

### 2. Experimental

### 2.1. Materials

Anhydrous 1,2-dichloromethane was obtained using a solvent purification system (Innovative Technologies). Anhydrous N,N-Dimethylformamide (DMF) was refluxed over CaH<sub>2</sub> and distilled in presence of molecular sieves. 1,2-Dichlorobenzene was distilled and degassed prior to use. All the bisphenols were purified by recrystallization in hexane. Grubbs catalyst bis(tricyclohexylphosphine)- benzylidineruthenium(IV) dichloride was obtained from Sigma Aldrich. All other chemicals were used as received from Tokyo Chemical Industry Co., Ltd. ADMET polymerization and hydrogenation were performed under nitrogen using standard Schlenk techniques.

### 2.2. Instrumentation

High temperature <sup>1</sup>H NMR (300 MHz) and <sup>13</sup>C NMR (75 MHz) spectra for saturated polymers were recorded on a Varian Associates Mercury 300 spectrometer, and <sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (100 MHz) spectra for monomers and unsaturated polymers were recorded on Bruker ARX400 spectrometer. Chemical shifts for <sup>1</sup>H and <sup>13</sup>C NMR were referenced to residual signals from CDCl<sub>3</sub> (<sup>1</sup>H:  $\delta$  = 7.26 ppm and <sup>13</sup>C:  $\delta$  = 77.23 ppm) or toluene-*d*<sup>8</sup> (<sup>1</sup>H:  $\delta$  = 7.09, 7.00, 6.98 and 2.09 ppm and <sup>13</sup>C:  $\delta$  = 137.86, 129.24, 128.33, 125.49 and 20.4 ppm). Thin layer chromatography (TLC) performed on EMD silica gel coated (250 µm thickness) glass plates was used to monitor all monomer synthesis. TLC plates were developed to produce a visible signature by both of ultraviolet light and iodine. FT-IR spectroscopy was also carried out for monomers, unsaturated and saturated polymers characterization.

Gel permeation chromatography (GPC) was performed at 150 °C using two columns (10 microns PD, 7.8 mm ID, 300 mm length) with HPLC grade 1,2,4-trichlorobenzene as the mobile phase at a flow rate of 1.0 mL/min. Injections were made at 0.3% w/v sample

concentration using a 150 µL injection volume. In the case of universal calibration, retention times were calibrated against narrow molecular weight polystyrene standards to produce number average molecular weight  $(M_n)$  and weight average molecular weight  $(M_w)$  values. Thermal gravimetric analysis (TGA) was performed using a TA Instruments O4000 series instruments with nitrogen purging rate set at 50 mL/min. Measurements were conducted from room temperature to 800 °C. DSC analysis was performed using a DSC equipped with a controlled cooling accessory at a heating rate of 10 °C/min unless otherwise noted. Transition temperatures were referenced to indium and freshly distilled noctane and transition enthalpies were referenced to indium. The samples were scanned for multiple cycles to remove recrystallization differences between the samples and the results reported were of the third scan in the cycle. XRD data were obtained on a Bruker D8 diffractometer, using the Cu K $\alpha$  radiation ( $\lambda = 0.15417$  nm) induced by a generator operating at 40 kV and 40 mA. Diffraction patterns were recorded for  $2\theta$ -values ranging from 5° to 60°.

### 2.3. Synthesis

### 2.3.1. Synthesis of 11-bromo-undec-1-ene

11-Undecen-1-ol (140 g, 0.82 mol) and CBr<sub>4</sub> (300 g, 0.90 mol) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (500 mL) in Schlenk flask and triphenylphosphine (237 g, 0.90 mol) was then added dropwise over 15 min at -5 °C. The system was stirred at -5 °C for 2 h, and raised to room temperature for 12 h. The solution was concentrated and a white precipitate formed which was removed by filtration. The resultant solution was fractionally distilled under reduced pressure to get a purified and colorless liquid product (177 g). Yield: 93%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 5.83 (ddt, *J* = 16.9, 10.1, 6.7 Hz, 1H), 4.98 (dd, *J* = 25.0, 13.6 Hz, 2H), 3.42 (t, *J* = 6.9 Hz, 2H), 2.06 (q, *J* = 6.9 Hz, 2H), 1.97–1.75 (m, 2H), 1.65–1.11 (m, 12H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 139.0, 114.1, 33.8, 33.7, 32.9, 29.4, 29.1, 28.9, 28.8, 28.2.

#### 2.3.2. General procedure for the synthesis of monomers

p-Benzenediol (Hydroquinone, defined as BP1 here) (2.2 g, 20 mmol) and sodium hydroxide (2.4 g, 60 mmol) were dissolved in 120 mL DMF in a 250-mL round bottomed Schlenk flask, then the mixture was stirred for 30 min, and a solution of 11-bromo-1undecene (12 g, 51.5 mmol) in DMF (120 mL) was added dropwise over 10 min. The resulting reaction mixture was heated at 70 °C and left stirring for more than 8 h. Subsequently, the reaction was cooled to RT and quenched with addition of diethyl ether (100 mL) and water (100 mL). The aqueous phase was extracted with diethyl ether (300 mL  $\times$  2), and the combined organic fractions were washed with brine and dried over MgSO<sub>4</sub> and concentrated. The residue was recrystallized from EtOH twice to obtain 6.1 g **BP1-M1**. Yield: 74%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta = 6.82$ (s, 2H), 5.93–5.70 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.23–4.72 (m, 2H), 3.90 (t, J = 6.6 Hz, 2H), 2.05 (q, J = 6.9 Hz, 2H), 1.84-1.64 (m, 2H),1.58 1.13 (m, 13H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 153.2, 139.2, 115.4, 114.1, 68.7, 33.8, 29.5, 29.4, 29.4, 29.4, 29.1, 28.9, 26.1.

### 2.3.3. General procedure for the synthesis of unsaturated homopolymers

Taking **BP1-M1** as example, **BP1-M1** (4 g, 9.66 mmol) was placed in a 25 mL flame dried Schlenk flask under nitrogen. Grubbs' first generation catalyst (79.5 mg, 1.0 mol %) was added and the mixture was stirred at 75 °C under high vacuum. The reaction flask was heated to 90 °C as it became viscous. After 48 h, the reaction was terminated by 5 mL vinyl ethyl ether. The polymer was precipitated by acidic methanol, filtered, washed with methanol and finally dried as a white solid, **BP1–P1** (3.6 g). Yield: 91%. <sup>1</sup>H

NMR (300 MHz, Toluene- $d^8$ , ppm):  $\delta = 6.83$  (s, 4H), 5.65–5.31 (m, 2H), 3.81 (t, J = 6.4 Hz, 4H), 2.23–2.11 (m, 5H), 1.80–1.61 (m, 4H), 1.57–1.18 (m, 19H). <sup>13</sup>C NMR (75 MHz, Toluene- $d^8$ , ppm):  $\delta = 154.5$ , 131.0, 130.4, 116.4, 69.4, 33.1, 30.3, 30.2, 30.0, 29.8, 26.7. GPC:  $M_n$ : 5300,  $M_w$ : 12,100, PDI: 2.3. TGA: 399 °C (5% weight loss). DSC:  $T_m$ : 81.8 °C, 103.9 °C.

# 2.3.4. General procedure for the hydrogenation of unsaturated homopolymers

Unsaturated polymer **BP1–P1** (2 g), *p*-toluenesulfonohydrazide (TSH) (4.5 mg, 24.2 mmol), tripropylamine (TPA) (3.47 mg, 24.2 mmol), were dissolved in 40-50 mL of p-xylene at a 100-mL Schlenk flask. The flask was placed in an oil bath set at 130 °C under vigorous stirring and N<sub>2</sub>. After 12 h, the reaction was cooling to room temperature and another supply of TSH and TPA was added, and the reaction was preceded for another 12 h. The viscous solution was poured into about 100 mL of cold methanol to obtain a white precipitate. After filtration and washed by *p*-xylene and cold methanol, 1.86 g **BP1-HP1** of polymer was obtained. Yield: 93%. <sup>1</sup>H NMR (300 MHz, Toluene- $d^{\hat{8}}$ , ppm):  $\delta = 6.93$  (s, 4H), 3.89 (t, *J* = 6.4 Hz, 4H), 3.89 (t, *J* = 6.4 Hz, 4H), 1.90–1.74 (m, 5H), 1.48 (dd, J = 22.0, 15.5 Hz, 38H). <sup>13</sup>C NMR (75 MHz, Toluene- $d^8$ , ppm):  $\delta = 154.2, 116.1, 69.1, 30.0, 29.9, 29.7, 26.4.$  GPC:  $M_{\rm n}$ : 5000,  $M_{\rm w}$ : 11,700, PDI: 2.3. TGA: 416 °C (5% weight loss). DSC:  $T_{\rm m}$ : 123.3 °C, 134.9 °C.

# 2.3.5. General procedure for the synthesis of unsaturated copolymers

The same method as described above for ADMET homopolymerization was used with a degassed solution of 1.38 g 1,9decadiene and 828 mg **BP1-M1** (1:5 = BP1-M1: 1,9-decadiene, monomer ratio) in 1,2-dichlorobenzene (2 mL) with 1.0 mol% Grubbs' first generation catalyst (10 mg). After 48 h of reaction, polymerization was terminated by adding the degassed ethyl vinyl ether (3 mL), and the solution was allowed to stir for 1 h. Then the solution was poured into acidic methanol to precipitate the polymer. The polymer was filtered, re-dissolved and re-precipitated two more times to remove the traces of catalyst. Polymer BP1dd-P7 (1.8 g) was recovered as a white solid. Yield: 91%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta = 6.81$  (s, 2H), 5.48–5.29 (m, 5H), 3.89 (t, J = 6.6 Hz, 2H), 2.14–1.84 (m, 10H), 1.83–1.68 (m, 2H), 1.68–1.50 (m, 2H), 1.50–1.16 (m, 27H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm):  $\delta = 153.2$ , 130.3, 129.9, 115.4, 68.7, 32.6, 32.5, 29.8, 29.6, 29.6, 29.5, 29.4, 29.3, 29.2, 29.0, 28.8, 28.7, 27.2, 26.1. GPC: M<sub>n</sub>: 2600, M<sub>w</sub>: 8600, PDI: 3.3. TGA: 419 °C (5% weight loss). DSC: *T*<sub>m</sub>: 33.6–66.6 °C.

# 2.3.6. General procedure for the hydrogenation of unsaturated copolymers

The same method described for **BP1-HP1** was used. 1.2 g of saturated polymer **BP1dd-HP7** was obtained. Yield: 96%. <sup>1</sup>H NMR (300 MHz, Toluene- $d^8$ , ppm):  $\delta = 6.93$  (s, 4H), 3.90 (t, J = 6.4 Hz, 4H), 2.24 (dt, J = 4.4, 2.2 Hz, 6H), 1.96–1.72 (m, 5H), 1.48 (s, 92H), 1.04 (t, J = 6.6 Hz, 3H). <sup>13</sup>C NMR (75 MHz, Toluene- $d^8$ , ppm):  $\delta = 154.2$ , 116.1, 69.1, 32.1, 30.0, 29.9, 29.7, 29.5, 26.4. GPC:  $M_n$ : 3500,  $M_w$ : 7000, PDI: 2.0. TGA: 422 °C (5% weight loss). DSC:  $T_m$ : 99.6 °C, 106.8 °C.

More synthesis procedures and NMR data of other products could be available in Supplementary Data.

### 3. Results and discussion

### 3.1. Synthesis and characterization of monomers and polymers

All the six monomers were synthesized via standard Williamson ether synthesis with sodium hydroxide or sodium hydride as the base in dry and air free DMF at 40 °C–65 °C. Subsequent ADMET polymerization with Grubbs' first generation catalyst were carried out in bulk polymerization, in 1,2-dichlorobenzene under vacuum for removing ethylene, or in CH<sub>2</sub>Cl<sub>2</sub> at 45 °C (Scheme 1). Grubbs' first generation was preferentially chosen for linear polymer with perfectly spaced aryl ether units. Considering hydrogenation catalyzed by Wilkinson's catalyst consumed long time under harsh condition, exhaustive hydrogenation by using tripropylamine and TsNHNH<sub>2</sub> (4-methylbenzene-sulfonhydrazide) was applied to all the nine polymers in *p*-xylene at 130 °C.

As shown in Scheme 1, we view the 3 as monomer, 4 as repeat units of unsaturated polymers, and 5 as the repeat unit of the desired saturated homopolymer. These aryl ether containing homopolymers could also be viewed as alternative copolymer of eicosane and aryl ether. From this point of view, it would be interesting if we would know the effect of sequence distribution and additional ethylene units on the structure-property relationship of ethylene copolymers with aryl ether, therefore we also synthesized monomers and random copolymers of ethylene with aryl ether as shown in Scheme 2. Previous work by Kenneth B. Wagener has demonstrated that ADMET random copolymerization of 1,9-decadiene with branched alkenes is an available method to change the density of branched alkyl units along the polymer's backbone [34], for which we chose three relatively typical monomers to copolymerize with 1,9-decadiene with the feeding ratio of 1:5 (monomer: 1,9-decadiene) (Scheme 2).

The obtained monomers and polymers were characterized by <sup>1</sup>H NMR and <sup>13</sup>C NMR. Monomer **BP1-M1** is featured with one distinct aromatic signal at 6.82 ppm, and the two signals of terminal alkenes appearing at 5.0 and 5.8 ppm (Fig. 1). The corresponding polymer **BP1-P1** exhibits signals of internal alkenes at 5.5 ppm (the *cis-trans* ratio of the internal alkenes was about 1:3), meanwhile, signals of the terminal alkene is invisible in the <sup>1</sup>H NMR spectrum, indicative of high molecular weight of unsaturated polymer. After exhaustive hydrogenation of the unsaturated polymer, **BP1-HP1** is characterized by complete disappearance of the signals of internals alkenes at 5.5 ppm. Similarly, other monomers and their corresponding unsaturated and saturated polymers were also confirmed by <sup>1</sup>H NMR. <sup>13</sup>C NMR shifts of series products of BPBP were studied (Fig. 2). Eight aromatic carbons appear at 157.1, 147.4, 139.0, 132.1, 131.1, 127.4, 125.8, and 113.2 ppm. The bridgehead carbon between the two phenyl groups appears at 63.6 ppm, upfield with increasing number of the aromatic ring attached directly. After polymerization, the terminal alkenes at 139.2 and 114.1 ppm disappear with the emergence of internal alkenes at 131.0 and 130.4 ppm. After exhaustive hydrogenation, the signals of internals alkenes at 131.0 and 130.4 ppm disappear completely.

The GPC data of saturated polymer were calculated and collected in Table 1, and GPC curve was also depicted in Supplementary Data Fig. S1. The series products of BPF were characterized by IR (Supplementary Data Fig. S2) and the ratio BP1-M1 to 1,9-decadiene was calculated via <sup>1</sup>H NMR (Supplementary Data Fig. S3), the integration of the aromatic ring at 6.8 ppm is compared with the integration of the olefin protons at 5.4 ppm, and the ratio is 1:2.69 in BP1dd-P7 (1:2.45 in BPFdd-P8 and 1:2.05 in **BPBPdd-P9**), which corresponds to an actually experimental reaction ratio of one BP1-M1 to 4.4 equivalent 1,9decadiene (this ratio is 1:3.9 for BPFdd-P8 and 1:3.1 for BPBPdd-P9). The final composition in the copolymers is deviation from the initial monomer feeding ratio, mainly due to different incorporation reactivities of two monomers, and an inevitable loss for 1,9-decadiene under vacuum should also be considered.



Scheme 1. Synthetic route of polyethylene periodically spaced with aromatic ether.

### 3.2. Thermal properties

Thermal properties of saturated polymers were systematically studied with TGA and DSC, and the data were collected in Table 1. Polymer decomposition temperatures ( $T_d$ ) were presented as the 5% weight loss temperature under nitrogen. Glass transition temperatures ( $T_g$ ), melting points ( $T_m$ ) and crystallization behaviors of these polymers were measured by DSC, all the samples were processed through a heating-cooling-heating procedure unless otherwise noted. The first heating runs from room temperature to the temperatures 30 °C above their melting points were performed to eliminate the thermal history of the samples. The actual heating curves and data came from the second heating runs.

The results of the cooling run are shown in Fig. 3(a), indicating a distinct single peak for all three polymers **BP1-HP1**, **BP2-HP2** and **BPF-HP4**. Surprisingly, the subsequent heating curves shown in Fig. 3(b) reveal unusual melting behaviors for these polymers. For example, **BP1-HP1** first melts at 123.3 °C, but then it crystallizes at

128 °C, and re-melts at 134.9 °C. **BPF-HP4** exhibits the similar behavior. In fact, this similar phenomenon has also been found in reported polymers [35,36], but here it still shows distinct features.

To explain this phenomenon, we propose two possible mechanisms. The first hypothesis involves the melting of the smaller imperfect crystals, followed by recrystallization to more perfect and larger crystals, and eventually the melting of these larger crystals at a higher temperature. The second hypothesis suggests transformation of crystal forms at elevated temperature, as one crystal form is melted at low temperatures, and the other form is crystallized and subsequently melted at high temperatures.

In order to verify the first hypothesis, we obtained the DSC curves of **BP1-HP1** as different heating rates. As shown in Fig. 4(b), the crystallizing peak of the heating run becomes bigger with decreasing heating rate. **BP2-HP2** exhibits similar behavior (Supplementary Data Fig. S4). On the other hand, as the heating rate increases, the crystallizing peak is diminishing, and completely disappears at the heating rate of 30 °C/min. We suspect that the



Scheme 2. Copolymerization and hydrogenation of random copolymers, BP1dd-HP7 (corresponding monomer BP1-M1), BPFdd-HP8 (corresponding monomer BPF-M4) and BPBPdd-HP9 (corresponding monomer BPBP-M6).



Fig. 1. <sup>1</sup>H NMR of BP1. (a) Monomer, BP1-M1, (b) Unsaturated polymer, BP1-P1, and (c) Saturated polymer, BP1-HP1.

large rigid aryl ether units restrict the movement of polymer chains, and if high cooling rate is applied, there may be no enough time for crystallizing, thus these units prevent polymers from forming larger crystals during the cooling run.

To provide evidence for the second hypothesis, **BP1-HP1** samples with three different thermal histories were prepared for XRD. **BP1-HP1-a** is collected after cooling run, **BP1-HP1-b** is quenched after annealing at 60 °C for 10 min, another sample **BP1-HP1-c** is quenched at 128 °C marked by asterisk in Fig. 3(b) where it accomplishes crystallization. If the crystal form transformation

hypothesis is valid, we expect that the sample **BP1-HP1-a** has both forms, sample **BP1-HP1-b** has mainly the first crystal form, and sample **BP1-HP1-c** has mostly the second crystal from. However, after XRD test as shown in Fig. 5, all three samples have the same orthorhombic unit cell structure with two characteristic crystallizing peaks observed at  $2\theta = 21.5^{\circ}$  and  $24.0^{\circ}$ , corresponding to reflection planes (110) and (200) respectively. Therefore, this sequence of melting/crystallization phenomenon should not be due to transformation of crystal forms. X-ray diffractograms for **BP2-HP2** and **BPF-HP4** were shown in Supplementary Data Fig. S5.



Fig. 2. <sup>13</sup>C NMR of BPBP. (a) Monomer, BPBP-M6, (b) Unsaturated polymer, BPBP-P6, and (c) Saturated polymer, BPBP-HP6.

 Table 1

 Summary of saturated polymer molecular weights and thermal properties.

Polymer	$T_{\rm m}~(^{\circ}{\rm C})^{\rm a}$	$T_{\rm g}(^{\circ}{\rm C})^{\rm a}$	$T_{d} (^{\circ}C)^{b}$	$M_n  (kDa)^c$	$M_{\rm w}({\rm kDa})^{\rm c}$	PDI
BP1-HP1	123.3, 134.9	_	416	5.0	11.7	2.3
BP2-HP2	128.2, 133.1	_	422	19.3	26.9	1.4
BPA-HP3	77.6, 90.4	_	411	6.7	18.1	2.7
BPF-HP4	127.2, 132.4	_	426	8.0	22.4	2.8
BPAP-HP5	_	-6	425	12.2	18.4	1.5
BPBP-HP6	_	20	406	10.4	19.8	1.9
BP1dd-HP7	99.6, 106.8	-	422	3.5	7.0	2.0
BPFdd-HP8	102.6	-	418	13.5	30.5	2.3
BPBPdd-HP9	88.4	-	430	5.6	13.6	2.4

<sup>a</sup> Determined via DSC, 10 °C/min scan rate, values determined from the second scan data,  $T_m$  is defined as the peak value,  $T_g$  is from the heating curve.

<sup>b</sup> Given as the 95% weight loss temperature, 10 °C/min.

<sup>c</sup> Determined via GPC (1 mL/min in trichlorobenzene) with curves shown in Supplementary Data Fig. S1, 3‰ concentration, using polystyrene calibration.

The melting behavior of **BPA-HP3** is similar with above samples, but the melting point of **BPA-HP3** (Fig. 6),  $T_{m2} = 90.4$  °C, is lower than that of **BP1-HP1**, **BP2-HP2** and **BPF-HP4**. This may be because that the two methyl groups inserted between the two phenyl rings in every aryl ether unit, reduces the effect from rigidity of the aryl



Fig. 3. DSC curves of BP1-HP1, BP2-HP2, and BPF-HP4. Cooling run (a) and heating run (b), 10  $^\circ\text{C}/\text{min}.$ 





Fig. 4. DSC curves of **BP1-HP1** in different scanning rate. Cooling run (a) and Heating run (b).

ether units and offers a relative better flexibility for the polymers. Therefore, the melting point is decreased. This trend from **BP1-HP1**, **BP2-HP2** and **BPF-HP4** to **BPA-HP3** indicates that methyl groups and methylene unit between the two phenyl groups have a large effect on the structure and thermal behavior of polymers.

DSC also reveals glass transitions temperatures ( $T_g$ ) of series polymers of **BPAP** and **BPBP** of Scheme 1. Unlike polymers discussed above, polymers of **BPAP** and **BPBP** show amorphous after the incorporation of one or two more aromatic rings (Supplementary Data Fig. S6). And hydrogenation brings the  $T_g$  up to high values. Glass transition temperature of polyethylene ranges from -150 °C to -50 °C [37], herein the ethylene-*co*-aryl ether polymers show higher  $T_g$  values than polyethylene, which is probably due to that rigid groups like these aryl ether units enhance the rigidity of polymers, thus the decreased flexibility leads to improving  $T_g$ .

The random copolymers exhibit  $T_g$  and  $T_m$  in a typical way (Fig. 7 and Supplementary Data Fig. S7). **BPFdd-P8** exhibits semicrystallinity with  $T_m = 40.6$  °C, and hydrogenation brings the  $T_m$  to 102.6 °C. However, **BPBPdd-P9** are amorphous with  $T_g = 8$  °C, which is higher than the corresponding unsaturated homopolymer **BPBP-P6** (Supplementary Data Fig. S6), and hydrogenation



**Fig. 5.** XRD of **BP1-HP1** after different heat treatment process, **BP1-HP1-a** is collected after cooling run, **BP1-HP1-b** is quenched after annealing at 60 °C for 10 min, another sample **BP1-HP1-c** is quenched at 128 °C marked by asterisk in Fig. 3(b) where it finishes crystallization.

transforms it to semicrystallinity with  $T_{\rm m} = 88.4$  °C. Not surprisingly, the copolymer **BPBPdd-HP9** exhibits semicrystallinity when the methylene distance is increased after the disappearance of internal alkenes since crystalline chain segments become longer. Both **BP1dd-HP7** and its corresponding unsaturated copolymer **BP1dd-P7** exhibit wide melting/crystallization range (Supplementary Data Fig. S8). This could possibly be caused by heterogeneous composition and the relatively low molecular weight of **BP1dd-P7** and **BP1dd-HP7**. Here, reducing the density of aryl ether units in the main chain of polymers weakens their effects on the thermal behaviors shown above, and ethylene segments exhibit an increasingly dominant influence.

By regulating the identity and distribution of the aryl ether units inserted in the main chains of polyethylene, promisingly, controlling of the melting point and secondary structures even the aggregation state of the new series of polymers could be achieved, which can be a reference for design of well-defined polymer to study the structure—property relationship.



Fig. 6. DSC of BPA-HP3 with 10 °C/min as heating and cooling rate.



Fig. 7. DSC curves of BPFdd-HP8 and BPBPdd-HP9.

Decomposition temperature ( $T_d$ ) of unsaturated polymers varied from 169 °C in **BPAP-P5** to 410 °C in some polymers (Supplementary Data Fig. S9), since it is possible that a small amount of solvent remains trapped within **BPAP-P5**, which could account for the lower  $T_d$  around the boiling point of 1,2dichlorobenzene (180.4 °C), and its  $T_d$  could be inferred as about 420 °C at 10% weight loss from the curve. Decomposition temperature ( $T_d$ ) of saturated polymers varied from 406 °C in **BPBP-HP6** to 430 °C in **BPBPdd-HP9** (Fig. 8). Other polymers displayed intermediate values. Overall, the polymers exhibited higher thermal stability on average than the commercial polyethylene with  $T_d$  of about 300 °C [38], which indicates that inserting such aryl ether units into the main chains of polyethylene has introduced the heat resistance property of poly (aryl ether) into polyethylene.

### 4. Conclusion

Ethylene-co-aryl ether polymers periodically containing a series of aryl ether units was successfully synthesized via ADMET polymerization followed by hydrogenation. The structure-property relationship has been systematically investigated by tuning the



Fig. 8. TGA traces of the saturated homopolymers and copolymers.

steric bulkiness of aryl ether units incorporated in the ethylene segment. Morphology of semicrystallinity to amorphous state was found by periodical insertion of larger aryl ether units into specific location in the main chain. BP1-HP1, BP2-HP2 and BPF-HP4 display a sequence of melting/crystallization phenomenon, irrelevance of the arvl ether units in the functional sites of main chain. Typical orthorhombic unit cell structure has been revealed by XRD in those semicrystallinity polymers. The more bulky aryl ether groups based BPA-HP3 exhibits a weak crystallization behavior, while polymers of **BPAP** and **BPBP** with more phenyl rings in every aryl ether units show amorphous state. Three random copolymers obtained from BP1-M1, BPF-M4, BPBP-M6 copolymerizing with 1,9-decadiene also exhibit semicrystallinity, as the longer ethylene segments were incorporated in the main chain of polymers. Notably, incorporation of these aryl ether units has also increased the thermal stability of polymers, demonstrating the heat resistance property of poly (aryl ether) was successfully introduced into polyethylene.

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### Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2015.03.039.

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