

## Synthesis and properties of novel poly(aryl ether ketone)s containing both diphenyl moiety and amide linkages in the main chains

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### ABSTRACT

New monomers, 4,4'-bis(4-phenoxybenzoyl)diphenyl (BPOBDP) and *N,N'*-bis(4-phenoxybenzoyl)-*p*-phenylenediamine (BPBPPD), were conveniently synthesized via simple synthetic procedures from readily available materials. A series of novel poly(aryl ether ketone)s containing both diphenyl moiety and amide linkages in the main chains were prepared by electrophilic Friedel–Crafts solution copolycondensation of isophthaloyl chloride (IPC) with a mixture of BPOBDP and BPBPPD, over a wide range of BPOBDP/BPBPPD molar ratios, in the presence of anhydrous AlCl<sub>3</sub> and *N*-methylpyrrolidone (NMP) in 1,2-dichloroethane (DCE). All the polymers are semicrystalline and had remarkably increased *T*<sub>g</sub>s over commercially available PEEK and PEKK due to the incorporation of the diphenyl moiety and amide linkages in the main chains. The polymers with 40–60 mol% BPBPPD had not only high *T*<sub>g</sub>s of 183–189 °C, but also moderate *T*<sub>m</sub>s of 314–328 °C, which are very suitable for the melt processing. These polymers had tensile strengths of 107.4–111.5 MPa, Young's moduli of 2.20–2.45 GPa, and elongations at break of 11.3–13.5% and exhibited high thermal stability and good resistance to organic solvents.

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### 1. Introduction

Poly(aryl ether ketone)s (PAEKs) are an important class of engineering thermoplastics possessing excellent mechanical properties, good environmental resistance, and high thermal and thermo-oxidative resistance [1–4]. Among them poly(ether ether ketone) (PEEK) and poly(ether ketone ketone) (PEKK) are the most widely used materials and have found many applications in aerospace, electronics and nuclear fields [5–7]. There are two general synthetic pathways to producing PAEKs [8–10]. The first approach is a synthesis involving nucleophilic aromatic substitution, in which a diaryl ether linkage is formed. The second one is a synthesis involving Friedel–Crafts electrophilic substitution, in which a diaryl ketone linkage is obtained. Normally, the preparation involving nucleophilic aromatic substitution is conducted at 300 °C and even higher temperatures. The electrophilic approach has been the popular method to prepare various kinds of poly(aryl ether ketone)s because the polymerization reaction conditions are mild and the monomers, which are used in the electrophilic route, have been more selective, cheaper, and readily available [11–16].

Drawbacks of poly(aryl ether ketone)s include their high cost and relatively low glass-transition temperatures. In advanced composite applications it is desirable to utilize poly(aryl ether ketone) materials with higher glass-transition temperatures.

Modification of poly(aryl ether ketone) properties is desired for many applications. On the other hand, the synthesis and investigation of novel poly(aryl ether ketone)s would be very useful for a more rigorous structure–property correlation of this very interesting class of polymers. Taking into account that poly(aryl ether ketone)s (e.g. PEEK) suffer from poor creep behavior above their relatively low glass transitions, the synthesis of semicrystalline poly(aryl ether ketone)s with increased *T*<sub>g</sub> is of high interest. In recent years, some papers were published concerning the copolymerization of PEEK in order to improve its glass-transition temperature (*T*<sub>g</sub>), and processability at high temperatures, and to obtain low-cost materials [17–20]. However, the improvement of *T*<sub>g</sub> is not so marked for those reported PEEK copolymers. Shibata et al. reported the synthesis of the block copolymers of the poly(ether ether ketone) (PEEK) and the poly(aryl ether sulfone) containing biphenylene moiety (PEBS) [21]. Although the degree of crystallinity of the PEEK/PEBS block copolymers decreased with the increase in PEBS content, the glass-transition temperature (*T*<sub>g</sub>) rose greatly, and superior heat resistance and good mechanical properties at high temperatures were obtained. It is well-known that

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incorporation of rigid and bulky groups such as diphenyl or naphthalene in the main chains leads to an increase in the temperature of the glass transition. Considerable attention has been devoted to the preparation of novel poly(aryl ether ketone)s containing diphenyl or naphthalene moieties due to their high-temperature performance [22–26]. Wu et al. [27] reported the synthesis of soluble aromatic poly(ether ketone)s containing diphenyl moieties and fluorine groups via a nucleophilic aromatic substitution polycondensation, all the polymers formed transparent, strong, and flexible films having low dielectric constants and low water absorptions. Guiver et al. [28] reported the synthesis of aromatic poly(ether ketone)s containing diphenyl moieties and sulfonic acid groups by a mild sulfonation method for proton exchange membranes. Zolotukhin et al. [12] reported the synthesis of naphthalene-containing poly(aryl ether ketone)s by the precipitation electrophilic polycondensation, the polymers obtained possessed high  $T_g$ s values ( $>180^\circ\text{C}$ ) and also too high  $T_m$ s values ( $>380^\circ\text{C}$ ), which made it difficult to process. To expand the application of PAEKs, their melt processabilities and thermal properties need to be improved by reducing the melting temperature and increasing the glass-transition temperature. Poly(aryl ether ketone)s containing both diphenyl moiety and amide linkages in the main chains are expected to combine high  $T_g$  values and the other attractive features of aromatic polyamides with the excellent chemical, solvent, and stress-crack resistance of the poly(aryl ether ketone)s. In this paper, we synthesized two new monomers, 4,4'-bis(4-phenoxybenzoyl)diphenyl (BPOBDP) and *N,N'*-bis(4-phenoxybenzoyl)-*p*-phenylenediamine (BPBPPD), via simple synthetic procedures from readily available materials. A series of novel poly(aryl ether ketone)s containing both diphenyl moiety and amide linkages in the main chains were prepared by the modified electrophilic Friedel–Crafts solution copolycondensation of isophthaloyl chloride (IPC) with a mixture of BPOBDP and BPBPPD, over a wide range of BPOBDP/BPBPPD molar ratios, in the presence of anhydrous  $\text{AlCl}_3$  and *N*-methylpyrrolidone (NMP) in 1,2-dichloroethane (DCE).

## 2. Experimental

### 2.1. Materials

All reagents and solvents were of analytical grade and were used without further purification unless stated otherwise. 4-Bromobenzoyl chloride and isophthaloyl chloride (IPC) (Shuanglin Chemical Co., China) were purified by distillation under vacuum prior to use. 1,2-Dichloroethane (DCE, Shanghai Chemical Reagent), *N*-methylpyrrolidone (NMP, Shanghai Chemical Reagent), *N,N*-dimethylacetamide (DMAc, Shanghai Chemical Reagent), *N,N*-dimethylformamide (DMF, Shanghai Chemical Reagent) and *o*-dichlorobenzene (Shanghai Chemical Reagent) were purified by distillation and dried by 0.4 nm molecular sieve. Aluminum chloride (Shanghai Chemical Reagent) was sublimed prior to use. *p*-Phenylenediamine (Shanghai Chemical Reagent), phenol

(Shanghai Chemical Reagent) and *p*-phenoxybenzoic acid (Shanghai Chemical Reagent) were used as received.

### 2.2. Measurements

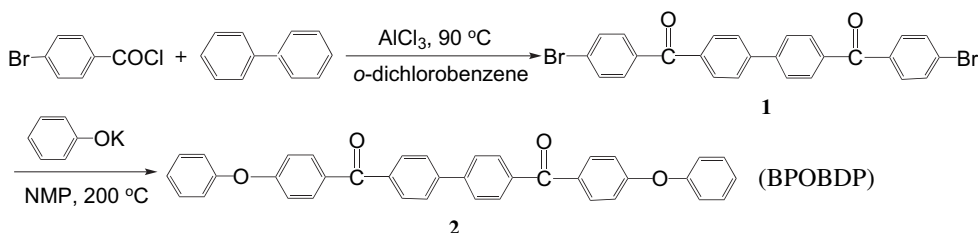
Elemental analysis was performed with Perkin–Elmer Model 2400 CHN analyzer. The FT-IR spectra of the monomers and polymers in KBr pellets (2%) were recorded using a Nicolet FT-IR (510P) spectrophotometer.  $^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) spectra were obtained with a Bruker PC-A400 (400 MHz) spectrometer at an operating temperature of  $25^\circ\text{C}$  using  $\text{DMSO-d}_6$  or  $\text{CDCl}_3/\text{CF}_3\text{CO}_2\text{H}$  as a solvent. Mass spectra were obtained on a Finnigan 4510 mass spectrometer. Inherent viscosities were obtained with a concentration of 0.2 g/dL in 95%  $\text{H}_2\text{SO}_4$  at  $25^\circ\text{C}$  using an Ubbelohde suspended level viscometer. Differential scanning calorimetry (DSC) measurements were performed on a Mettler Toledo DSC 821e instrument at a heating rate of  $10^\circ\text{C}/\text{min}$  under nitrogen. The glass-transition temperature ( $T_g$ ) was taken in DSC curve as the center of the step transition in the second heating run. Thermogravimetric analysis (TGA) was performed on a Netzsch Sta 449c thermal analyzer system at a heating rate of  $10^\circ\text{C}/\text{min}$  in nitrogen. The mechanical properties were measured at  $25^\circ\text{C}$  using a Shimadzu AG-2000A tester at a crosshead speed of 5 mm/min. The samples are dog bone shape and have dimensions of  $2.0 \times 4.0 \times 20 \text{ mm}^3$ . The temperatures for the polymers to process are  $20^\circ\text{C}$  higher than the  $T_m$ s. At least five samples for each polymer were tested, and the average value was reported. Wide-angle X-ray diffraction (WAXD) was measured with a Rigaku D/MAX-IIA X-ray diffractometer, using  $\text{CuK}\alpha$  radiation, at 30 kV and 20 mA. The diffractograms were recorded at  $25^\circ\text{C}$  over the range of  $10$ – $40^\circ$ . Samples were powder.

### 2.3. Monomer synthesis

#### 2.3.1. Synthesis of 4,4'-bis(4-bromobenzoyl)diphenyl (**1**)

To a 100 mL round-bottomed flask was added 4-bromobenzoyl chloride (24.15 g, 0.11 mol), diphenyl (7.7 g, 0.05 mol), anhydrous powdered aluminum chloride (20 g, 0.15 mol) and *o*-dichlorobenzene (60 mL) with stirring under nitrogen at  $0^\circ\text{C}$ . The suspension was stirred at room temperature for 1 h and at  $90^\circ\text{C}$  for 8 h. The reaction mixture was poured into cold aqueous hydrochloric acid, then the water was decanted off and the residue was washed with water several times. Next, methanol was added to the oily residue to precipitate a solid. Finally, the crude product was recrystallized from DMF and dried under vacuum at  $100^\circ\text{C}$  to afford 21.5 g of white crystals (**1**).

Yield: 83%. m.p.:  $338$ – $339^\circ\text{C}$ . IR (KBr,  $\text{cm}^{-1}$ ): 1647, 1605, 1583, 852, 749;  $^1\text{H}$  NMR ( $\text{DMSO-d}_6$ ,  $\delta$ , ppm): 7.90 (d,  $J = 8.4 \text{ Hz}$ , 4H), 7.77 (d,  $J = 8.4 \text{ Hz}$ , 4H), 7.72 (d,  $J = 8.4 \text{ Hz}$ , 4H), 7.66 (d,  $J = 8.4 \text{ Hz}$ , 4H); MS (EI, 70 eV):  $m/z$  522 ( $\text{M}^+$ ,  $^{81}\text{Br}$ , 18), 520 ( $\text{M}^+$ , 35), 518 ( $\text{M}^+$ ,  $^{79}\text{Br}$ , 17), 363 (48), 185 (97), 183 (100), 152 (46), 76 (42). Anal. Calcd. for  $\text{C}_{26}\text{H}_{16}\text{O}_2\text{Br}_2$ : C, 60.01; H, 3.10. Found: C, 59.73; H, 2.88.



Scheme 1. Synthesis of 4,4'-bis(4-phenoxybenzoyl)diphenyl (BPOBDP).

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