



# Synthesis and characterization of soluble aromatic poly(ether amide amide ether ketone ketone)s by electrophilic Friedel–Crafts solution polycondensation

Mingzhong Cai \*, Meihua Zhu, Yongfeng Sun, Jiangping Qian

Department of Chemistry, Jiangxi Normal University, Nanchang 330022, China

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## ABSTRACT

A new monomer, *N,N*-bis(4-phenoxybenzoyl)-*m*-phenylenediamine (BPBMPD), was prepared by condensation of *m*-phenylenediamine with 4-phenoxybenzoyl chloride in *N,N*-dimethylacetamide (DMAC). Novel soluble aromatic poly(ether amide amide ether ketone ketone)s (PEAAEKs) were synthesized by electrophilic Friedel–Crafts solution copolycondensation of BPBMPD with a mixture of terephthaloyl chloride (TPC) and isophthaloyl chloride (IPC) in the presence of anhydrous aluminum chloride and *N*-methylpyrrolidone (NMP) in 1,2-dichloroethane (DCE). The influences of reaction conditions on the preparation of polymers were examined. The polymers obtained were characterized by different physico-chemical techniques such as FT-IR, DSC, TGA, and wide-angle X-ray diffraction (WAXD). All the polymers were amorphous and the solubility of the polymers was improved by the incorporation of 1,3-dibenzoylaminobenzene moieties in the main chain. Thermal analyses showed that the polymers had high  $T_g$ s of 220–231 °C and exhibited high thermal stability. All the polymers formed transparent, strong, and flexible films, with tensile strengths of 102.9–108.5 MPa, Young's moduli of 2.44–2.86 GPa, and elongations at break of 9.8–13.7%.

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## 1. Introduction

Poly(aryl ether ketone)s (PAEKs), including poly(ether ether ketone) (PEEK), poly(ether ketone ketone) (PEKK), and poly(ether ether ketone ketone) (PEEKK), are a family of high-performance engineering thermoplastics, which are used in aerospace, electronics and nuclear fields [1–5]. Their excellent mechanical, thermo-oxidative, electrical and chemical resistance properties make them candidates for advanced materials [6–10]. There are two general synthetic pathways to producing PAEKs [11–13]. The first approach is a synthesis involving nucleophilic aromatic substitution, in which a diaryl ether linkage is formed [14–18]. The second one is a synthesis involving Friedel–Crafts electrophilic substitution, in which a diaryl ketone linkage is obtained [19–25]. In general, nucleophilic aromatic substitution is more selective than Friedel–Crafts electrophilic aromatic substitution. However, certain polyacylation reactions were also shown to be very selective. Some of them were used in the development of such polymers as “Stilan” (Rychem), “Declar” (Dupont), “Ultrapek” (BASF). Drawbacks of

**Abbreviations:** BPBMPD, *N,N*-bis(4-phenoxybenzoyl)-*m*-phenylenediamine; PEAAEKs, poly(ether amide amide ether ketone ketone)s; TPC, terephthaloyl chloride; IPC, isophthaloyl chloride; DCE, 1,2-dichloroethane; PAEKs, poly(aryl ether ketone)s; PEEK, poly(ether ether ketone); PEKK, poly(ether ketone ketone); PEEKK, poly(ether ether ketone ketone).

\* Corresponding author. Fax: +86 791 8120388.

E-mail address: [caimzhong@163.com](mailto:caimzhong@163.com) (M. Cai).

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. In fact, it is difficult for PAEKs to be used as thin films and coatings because they have low solubility in almost all known solvents except for concentrated sulfuric acid and chloroform–trifluoroacetic acid mixtures. A great deal of research on PAEKs has been concentrated on the introduction of pendant groups to improve the solubility, processability, and other desired properties. To meet various demands without thermal stability being sacrificed, PAEKs with phenyl, methyl, butyl, and bromomethyl side groups have been successfully prepared [15,26–28]. Recently, poly(aryl ether ketone)s with trifluoromethyl-substituted benzene in the side chain have also been reported [29–31]. To the best of our knowledge, the synthesis of aromatic poly(ether amide amide ether ketone ketone)s by electrophilic polycondensation has not been reported in the open literature. Aromatic poly(ether amide amide ether ketone ketone)s are expected to combine high  $T_g$  values and the other attractive features of aromatic polyamides with the excellent chemical and stress-crack resistance of the poly(aryl ether ketone)s. In this paper, we synthesized a new

monomer containing amide linkages, *N,N'*-bis(4-phenoxybenzoyl)-*m*-phenylenediamine (BPBMPD). Novel aromatic poly(ether amide ether ketone)s (PEAAEKs) were prepared by electrophilic Friedel–Crafts solution copolycondensation of BPBMPD with a mixture of terephthaloyl chloride (TPC) and isophthaloyl chloride (IPC) in the presence of anhydrous aluminum chloride 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. Terephthaloyl chloride (TPC) 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), and *N,N*-dimethylformamide (DMF, 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. *m*-Phenylenediamine (Shanghai Chemical Reagent) and *p*-phenoxybenzoic acid (Shanghai Chemical Reagent) were used as received.

### 2.2. Synthesis of *N,N'*-bis(4-phenoxybenzoyl)-*m*-phenylenediamine (BPBMPD)

To a 250 mL, round-bottomed flask were added 14.98 g (0.07 mol) of 4-phenoxybenzoic acid, 50 mL of SOCl<sub>2</sub>, and 1 mL of DMF. The mixture was stirred at reflux temperature for 4 h. After removal of SOCl<sub>2</sub> under reduced pressure, the residue was dissolved in 180 mL of DMAc under nitrogen, then 3.24 g (0.03 mol) of *m*-phenylenediamine was added at 0 °C with stirring. The reaction mixture was stirred at 0 °C for 1 h and at room temperature for 4 h, poured into water (100 mL). The solid product was filtered and washed with water and ethanol, respectively. The crude product was recrystallized from DMF and ethanol ( $V_{\text{DMF}}/V_{\text{EtOH}} = 1/2$ ) and dried under vacuum at 100 °C to afford 12.06 g of white crystals.

(Yield: 80%. m.p. 225–226 °C. MS (EI):  $m/z$  (%) = 500 ( $M^+$ , 30), 197 (100). Elem. Anal. C<sub>32</sub>H<sub>24</sub>N<sub>2</sub>O<sub>4</sub> Calcd. C 76.79, H 4.83, N 5.59; Found. C 76.60, H 4.96, N 5.44. FTIR (KBr, cm<sup>-1</sup>): 3335, 1642, 1590, 1538, 1496, 1408, 1248, 846. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, δ, ppm): δ = 10.32 (s, 2H), 8.27 (s, 1H), 7.98 (d,  $J = 8.8$  Hz, 4H), 7.47–7.43 (m, 6H), 7.31 (t,  $J = 8.0$  Hz, 1H), 7.22 (t,  $J = 7.6$  Hz, 2H), 7.10 (d,  $J = 8.0$  Hz, 4H), 7.07 (d,  $J = 8.8$  Hz, 4H). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, δ, ppm): δ = 164.77, 159.77, 155.39, 139.11, 130.30, 129.92, 129.26, 128.63, 124.44, 119.55, 117.32, 115.96, 112.75.

### 2.3. Polymer synthesis

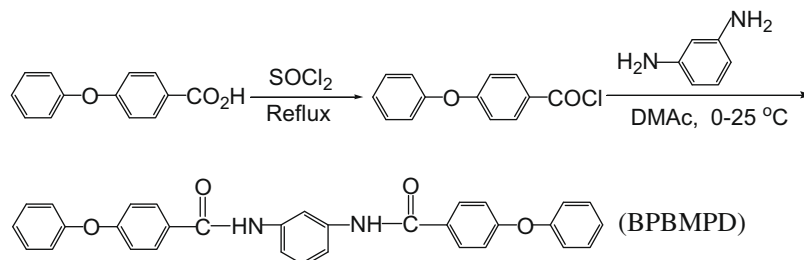
Poly(ether amide ether ketone)s (PEAAEKs) were prepared as shown in Scheme 2 by electrophilic Friedel–

Crafts solution copolycondensation of BPBMPD with a mixture of terephthaloyl chloride (TPC) and isophthaloyl chloride (IPC) in the presence of anhydrous aluminum chloride and NMP in DCE. A typical preparative procedure for polymer I is described hereafter. Other polymers were also obtained in a similar manner.

To a 150 mL, three-necked, round-bottomed flask equipped with a mechanical stirrer, a thermometer, nitrogen inlet and outlet tubes, were added 6.14 g (46 mmol) of anhydrous AlCl<sub>3</sub> and 20 mL of DCE. The flask was cooled to 0 °C using an ice-water bath, then a solution of 1.7 mL (18 mmol) of NMP in DCE (10 mL) was added dropwise with stirring over a period of 10 min and the mixture was stirred for 30 min and then cooled to –15 °C. Into the resulting suspension were added 2.50 g (5 mmol) of BPBMPD and 1.015 g (5 mmol) of TPC with stirring and the reaction mixture was warmed to 20 °C over 2 h and the reaction was continued at this temperature for 18 h. The reaction mixture was treated with 0.5 mL of diphenyl ether (DPE) as the end-capper for 1 h, quenched with methanol (50 mL) at 0 °C and the precipitate was crushed, washed with methanol and extracted with boiling methanol for 24 h and allowed to dry in air. The air-dried product was heated at 100 °C overnight under vacuum to give the polymer I. Yield: (94.4%). IR (KBr, cm<sup>-1</sup>): 3064, 3427, 1657, 1592, 1497, 1418, 1240, 844. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, δ, ppm): δ = 10.34 (s, 2H), 8.34 (s, 1H), 8.08 (d,  $J = 8.4$  Hz, 4H), 7.90–7.87 (m, 8H), 7.49 (d,  $J = 8.0$  Hz, 2H), 7.33–7.27 (m, 5H), 7.22 (d,  $J = 8.4$  Hz, 4H).

### 2.4. 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. <sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (100 MHz) spectra were obtained with a Bruker PC-A400 (400 MHz) spectrometer at an operating temperature of 25 °C using DMSO-d<sub>6</sub> as a solvent. Mass spectra were obtained on a Finnigan 4510 mass spectrometer. Inherent viscosities were obtained with a concentration of 0.5 g/dL in NMP at 25 °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 °C/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 °C/min in nitrogen. The polymer thin films for stress–strain tests and X-ray diffraction measurements were cast from NMP solutions onto glass plates, and this was followed by evaporation of the solvent and drying at 100 °C for 1 h, at 150 °C for 1 h, and at 200 °C in vacuo for 2 h. The completeness of the solvent removal from the films was confirmed by TGA and DSC measurements. The mechanical properties were measured at 25 °C using a Shimadzu AG-2000A tester at a crosshead speed of 10 mm/min and an average of at least three replicas was used. Wide angle X-ray diffraction (WAXD) was measured with a Rigaku D/MAX-IIA X-ray diffractometer, using CuKα



Scheme 1. Synthesis of BPBMPD.

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