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

Mingzhong Cai^{a,*}, Meihua Zhu^a, Pingping Wang^b, Caisheng Song^a

^a Department of Chemistry, Jiangxi Normal University, Nanchang 330022, PR China
^b Department of Chemistry, Jiujiang University, Jiujiang 332000, PR China

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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 copoly-condensation 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 AlCl₃ and *N*-methylpyrrolidone (NMP) in 1,2-dichloroethane (DCE). All the polymers are semicrystalline and had remarkably increased T_{gS} 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_{gS} of 183–189 °C, but also moderate T_{mS} 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].

* Corresponding author. Fax: +86 (791) 8120388. *E-mail address:* caimzhong@163.com (M. Cai).

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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_g 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_g) , and processability at high temperatures, and to obtain low-cost materials [17-20]. However, the improvement of T_{g} 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_g) rose greatly, and superior heat resistance and good mechanical properties at high temperatures were obtained. It is well-known that





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 hightemperature 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_{gs} values (>180 °C) and also too high T_{ms} values (>380 °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 $T_{\rm g}$ 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 AlCl₃ 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. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were obtained with a Bruker PC-A400 (400 MHz) spectrometer at an operating temperature of 25 °C using DMSO-d₆ or CDCl₃/CF₃CO₂H 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% H₂SO₄ at 25 °C using an Ubbelhode 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 Netzch Sta 449c thermal analyzer system at a heating rate of 10 °C/min in nitrogen. The mechanical properties were measured at 25 °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 $2.0 \times 4.0 \times 20$ mm³. The temperatures for the polymers to process are 20 °C higher than the *T*_ms. 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 CuKa radiation, at 30 kV and 20 mA. The diffractograms were recorded at 25 °C over the range of 10-40°. 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 °C. The suspension was stirred at room temperature for 1 h and at 90 °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 °C to afford 21.5 g of white crystals (1).

Yield: 83%. m.p.: 338–339 °C. IR (KBr, cm⁻¹): 1647, 1605, 1583, 852, 749; ¹H NMR (DMSO-d₆, δ , ppm): 7.90 (d, *J* = 8.4 Hz, 4H), 7.77 (d, *J* = 8.4 Hz, 4H), 7.72 (d, *J* = 8.4 Hz, 4H), 7.66 (d, *J* = 8.4 Hz, 4H); MS (EI, 70 eV): *m/z* 522 (M⁺, ⁸¹Br, 18), 520 (M⁺, 35), 518 (M⁺, ⁷⁹Br, 17), 363 (48), 185 (97), 183 (100), 152 (46), 76 (42). Anal. Calcd. for C₂₆H₁₆O₂Br₂: C, 60.01; H, 3.10. Found: C, 59.73; H, 2.88.



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



Scheme 2. Synthesis of N,N'-bis(4-phenoxybenzoyl)-p-phenylenediamine (BPBPPD).

2.3.2. Synthesis of 4,4'-bis(4-phenoxybenzoyl)diphenyl (2)

A 100 mL, three-necked, round-bottomed flask equipped with a mechanical stirrer, a nitrogen inlet, a Dean-Stark trap equipped with a condenser and a nitrogen outlet was charged with a mixture of phenol (3.76 g, 0.04 mol), potassium hydroxide (1.91 g, 0.034 mol), potassium carbonate (0.83 g, 0.006 mol), toluene (30 mL) and NMP (50 mL). The reaction mixture was heated to 140 °C until no further water was azeotropically distilled from the reaction mixture, then the temperature was raised to 170 °C to remove toluene. After being cooled to 40 °C, 4,4'-bis(4bromobenzoyl)diphenyl (1) (9.36 g, 0.018 mol) and copper powder (0.1 g) were added and the reaction mixture was heated to 200 °C and stirred at that temperature for 6 h. After cooling to room temperature, the product was precipitated from water. The solid product was washed with hot water several times, recrystallized from DMF and dried under vacuum at 100 °C to afford 8.25 g of white crystals (2).

Yield: 84%. m.p.: 280–281 °C. IR (KBr, cm⁻¹): 3065, 1644, 1605, 1591, 1492, 1266, 853, 755; ¹H NMR (DMSO-d₆, δ , ppm): 7.96 (d, J = 8.0 Hz, 4H), 7.88–7.84 (m, 8H), 7.52–7.47 (m, 4H), 7.28–7.25 (m, 2H), 7.18 (d, J = 8.0 Hz, 4H), 7.13 (d, J = 8.8 Hz, 4H); ¹³C NMR (CDCl₃/CF₃CO₂H, δ , ppm): 201.12, 163.99, 154.53, 144.95, 136.17, 133.81, 131.27, 130.08, 129.86, 127.44, 125.33, 120.52, 116.95; MS (EI, 70 eV): m/z 546 (M⁺, 33), 197 (100). Anal. Calcd. for C₃₈H₂₆O₄: C, 83.50; H, 4.79. Found: C, 83.23; H, 4.61.

2.3.3. Synthesis of N,N'-bis(4-phenoxybenzoyl)-pphenylenediamine (BPBPPD)

To a 250 mL, round-bottomed flask was added 4-phenoxybenzoic acid (14.98 g, 0.07 mol), 50 mL of SOCl₂, and 1 mL of DMF. The mixture was stirred at reflux temperature for 4 h. After removal of SOCl₂ under reduced pressure, the residue was dissolved in 180 mL of DMAc under nitrogen, then *p*-phenylenediamine (3.24 g, 0.03 mol) 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 dried under vacuum at 100 °C to afford 13.26 g of white crystals.

Yield: 88%. m.p.: 334–335 °C. IR (KBr, cm⁻¹): 3333, 1648, 1589, 1548, 1489, 1404, 1252, 846; ¹H NMR (DMSO-d₆, δ , ppm): 10.23 (s, 2H), 7.96 (d, *J* = 8.8 Hz, 4H), 7.69 (s, 4H), 7.44 (t, *J* = 8.0 Hz, 4H), 7.21 (t, *J* = 7.6 Hz, 2H), 7.08 (d, *J* = 9.2 Hz, 4H), 7.06 (d, *J* = 9.2 Hz, 4H); ¹³C NMR (DMSO-d₆, δ , ppm): 165.08, 160.22, 155.94, 135.22, 130.79, 130.32, 129.81, 124.92, 121.10, 120.03, 117.87; MS (EI, 70 eV): *m/z* 500 (M⁺, 27), 197 (100). Anal. Calcd. for C₃₂H₂₄N₂O₄: C, 76.79; H, 4.83; N, 5.59. Found: C, 76.53; H, 4.98; N, 5.47.

2.4. Synthesis of polymers

To a 100 mL, three-necked, round-bottomed flask equipped with a mechanical stirrer, a thermometer, nitrogen inlet and outlet tubes, was added anhydrous AlCl₃ (6.54 g, 49 mmol) and DCE (20 mL). The flask was cooled to 0 °C using an ice-water bath, then a solution of NMP (2 mL, 21 mmol) 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 BPBPPD (1.250 g, 2.5 mmol), BPOBDP (1.365 g, 2.5 mmol) and IPC (1.015 g, 5 mmol) 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 VI. Other polymers were also obtained by varying the molar ratio of BPOBDP to BPBPPD in a similar manner.



m/n = 0/100, 10/90, 20/80, 30/70, 40/60, 50/50, 60/40, 70/30, 80/20, 100/0

Scheme 3. Synthesis of polymers.

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Table 1

Effect of AlCl₃ quantity on polymerization.^a

AlCl ₃ (molar ratio to IPC)	Yield (%)	$\eta_{inh}^{b} (dL/g)$
8.2	89.7	0.19
8.8	91.6	0.58
9.2	93.7	0.91
9.8	94.3	1.13
10.2	94.5	1.09
10.6	94.2	0.89
11.0	93.9	0.78

 $^a\,$ Polymerized at 20 $^\circ$ C with 2.5 mmol of BPOBDP, 2.5 mmol of BPBPPD, 5 mmol of IPC, and 21 mmol of NMP in 30 mL of DCE for 20 h.

 $^{\rm b}$ Measured with a concentration of 0.2 g/dL in 95% sulfuric acid at 25 °C.

3. Results and discussion

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

The route to the synthesis of 4,4'-bis(4-phenoxybenzoyl)diphenyl (BPOBDP) (2), was shown in Scheme 1. The precursor 1 was conveniently obtained by Friedel-Crafts acylation reaction of 4-bromobenzoyl chloride and diphenyl in o-dichlorobenzene at 90 °C. The condensation of **1** with phenol for the preparation of **2** was carried out in NMP in the presence of potassium hydroxide and potassium carbonate at 200 °C. 4.4'-Bis(4-phenoxybenzoyl)diphenyl (2) was obtained as a pure material after recrystallization from DMF. FT-IR, NMR, MS spectroscopies and elemental analysis were used to confirm the structure of compound 2. In the IR spectrum, the key structural features include the following absorptions: aromatic C–H, 3065 cm⁻¹, aromatic ketone C=0, 1644 cm^{-1} , and aromatic ether Ar-O-Ar, 1266 cm⁻¹. From the ¹H NMR and ¹³C NMR spectra of compound **2**, all the signals corresponding to the proposed structure can be clearly observed.

3.2. Synthesis of N,N'-bis(4-phenoxybenzoyl)-p-phenylenediamine (BPBPPD)

As shown in Scheme 2, the new monomer containing amide linkages, *N*,*N*'-bis(4-phenoxybenzoyl)-*p*-phenylenediamine (BPBPPD), was conveniently prepared by the condensation reaction of *p*-phenylenediamine with 4-phenoxybenzoyl chloride in DMAc at 0–25 °C and could be obtained as a pure material after recrystallization from DMF. FT-IR, NMR, MS spectroscopies and elemental analysis were used to confirm the structure of BPBPPD. In the IR spectrum, the key structural features include the following absorptions: N–H stretch, 3333 cm⁻¹, amide C=O stretch, 1648 cm⁻¹, amide C–N stretch, 1404 cm⁻¹, and Ar–O–Ar stretch, 1252 cm⁻¹. The ¹H NMR and ¹³C NMR spectra of BPBPPD were in accordance with the proposed structure.

Table 2	
Effect of NMP	quantity on polymerization. ^a

NMP (molar ratio to IPC)	Yield (%)	$\eta_{inh}^{b} (dL/g)$
0	91.5	0.37
2.4	93.8	0.66
3.0	94.1	0.83
3.6	94.4	0.97
4.2	94.3	1.13
4.8	93.9	1.04
5.4	94.8	0.88

^a Polymerized at 20 °C with 2.5 mmol of BPOBDP, 2.5 mmol of BPBPPD, 5 mmol of IPC, and 28 mmol of AlCl₃ in 30 mL of DCE for 20 h. In addition, one molar equivalent of AlCl₃ relative to NMP was required to form a 1:1 complex of AlCl₃ and NMP.

^b Measured with a concentration of 0.2 g/dL in 95% sulfuric acid at 25 °C.

Table	3
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Effect of monomer concentration on polymerization.^a

Monomer concentration (mol/L)	Yield (%)	$\eta_{inh}{}^{b} (dL/g)$
0.33	93.5	0.56
0.25	93.9	0.83
0.20	94.1	1.05
0.17	94.3	1.13
0.14	94.0	1.08
0.12	94.6	0.93
0.10	93.5	0.77

^a Polymerized at 20 °C with 2.5 mmol of BPOBDP, 2.5 mmol of BPBPPD, 5 mmol of IPC, 21 mmol of NMP, and 49 mmol of AlCl₃ for 20 h.

^b Measured with a concentration of 0.2 g/dL in 95% sulfuric acid at 25 °C.

3.3. Synthesis and characterization of polymers

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, as shown in Scheme 3. It is generally accepted that premature polymer precipitation from initially homogeneous solution in Friedel-Crafts acylation polycondensation syntheses prevents further macromolecular chain growth reactions and produces polymer of undesirably low molecular weight and of poor thermal stability. Furthermore, such precipitation Friedel-Crafts polymerization generally produces an intractable product difficult to remove from the reaction vessel and to purify. It is well-known that ortho substitution and alkylation of the polymer in electrophilic polymerizations are more likely to occur if the reaction is conducted at elevated temperatures for a relatively long time [29].

Janson et al. [30] have reported that the Friedel-Crafts polymerization reaction can be controlled by the addition of a controlling agent to obtain the desired melt-processable, high molecular weight, substantially linear poly(aryl ether ketone)s. The controlling agent can efficiently suppress undesirable side reactions such as ortho substitution of activated aryloxy groups and alkylation of the polymer, which can lead to branching or cross-linking. Suppression of side reactions results in a thermally stable polymer that does not degrade or cross-link when subjected to elevated temperatures, e.g. temperatures above the melting point of the polymer for a period of time. Preferred controlling agents for the electrophilic polymerization reaction are organic Lewis bases such as DMF, DMAc and NMP. The 1:1 complex of Lewis acid (AlCl₃)/ Lewis base appears to act as a solvent for the polymer/Lewis acid complex formed during the reaction, thereby maintaining the polymer in solution or in a reactive gel state. Furthermore, the

Table 4	
Polymerization	results

Polymer	BPOBDP (mol%)	BPBPPD (mol%)	Yield (%)	$\eta_{inh}{}^{b}(dL/g)$
Ι	0	100	94.8	1.59
II	10	90	94.5	1.52
III	20	80	95.0	1.34
IV	30	70	94.1	1.30
V	40	60	94.9	1.19
VI	50	50	94.3	1.13
VII	60	40	95.2	1.08
VIII	70	30	94.3	0.94
IX	80	20	95.1	0.87
Х	100	0	94.0	0.79

 a Polymerized at 20 $^\circ C$ with 5 mmol of IPC, 5 mmol of (BPOBDP + BPBPPD), 21 mmol of NMP, and 49 mmol of AlCl_3 in 30 mL of DCE for 20 h.

 $^{\rm b}$ Measured with a concentration of 0.2 g/dL in 95% sulfuric acid at 25 °C.



Fig. 1. FT-IR spectrum of the polymer VI.

reaction mixture is more tractable, making work up of the polymer easier and ensuring effective removal of catalyst residues during purification.

Initially, in order to optimize polymerization reaction conditions, the influences of catalyst quantity, Lewis base quantity and monomer concentration on the preparation of the polymers were examined by Friedel-Crafts acylation of IPC with 50 mol% BPOBDP and 50 mol% BPBPPD in 1,2-dichloroethane using anhydrous AlCl₃ as a catalyst and NMP as a Lewis base. The preparation of PAEKs by electrophilic Friedel-Crafts acylation polycondensation generally starts at low temperature. The initial low temperature is necessary for controlling the reaction rate. A reaction temperature of about $-15 \,^{\circ}\text{C}$ to $-5 \,^{\circ}\text{C}$ has been found to be particularly effective. Thereafter, the reaction temperature is slowly increased and continued at room temperature. Concentration of the catalyst is an important factor for preparation of high molecular weight PAEKs. Because the carbonyl groups of the reactants and the reaction products are complexed with AlCl₃, and thereby deactivate it, AlCl₃ is generally employed at more than one equivalent of carbonyl groups in the reaction medium [31,32]. The optimum ratio of AlCl₃ to carbonyl group was reported to be 1.35-1.45 [11,33]. In our modified Friedel-Crafts acylation polycondensation, an additional amount of AlCl₃ was needed for the formation of a 1:1 complex of AlCl₃ and NMP due to the addition of Lewis base (NMP) as the controlling agent. Table 1 shows the effect of the AlCl₃/IPC feed ratio on the inherent viscosity of the polymer obtained. The polymerization reaction with 8.2 equivalents of AlCl₃ to IPC afforded a polymer with a low inherent viscosity of 0.19 dL/g due to the absence of a catalytic amount of AlCl₃. At least a molar equivalent excess of AlCl₃ over the monomer was necessary to obtain polymers with a higher viscosity. The inherent viscosity of the polymer increased with the increase in concentration of AlCl₃. When the molar ratio of AlCl₃ to IPC was in the range of between 9.2 and 10.6, a polymer with high inherent viscosity (>0.89 dL/g) could be obtained. However, a large excess of AlCl₃, for example, a elevenfold excess, resulted in a decreased inherent viscosity of the polymer. Therefore, a suitable quantity of AlCl₃ was about ten molar equivalents relative to IPC.

The effect of Lewis base (NMP) quantity on polymerization was also investigated and the results are summarized in Table 2. As shown in Table 2, the precipitation polycondensation reaction without NMP afforded a polymer with a lower inherent viscosity of 0.37 dL/g. The inherent viscosity of the polymer increased with the increase in molar ratios of NMP to IPC from 2.4 to 4.2 due to maintaining the polymer in solution or in a reactive gel state, but further increasing the quantity of NMP resulted in a decrease in

inherent viscosity of the polymer because of the decrease in the rate of polymerization reaction. So, an optimum quantity of NMP was about 4.2 molar equivalents relative to IPC.

The Friedel–Crafts acylation polymerization also showed a characteristic effect of monomer concentration on the inherent viscosity of polymers. Table 3 shows the influence of monomer concentration on the polymer viscosity in the course of preparation of the polymers. As shown in Table 3, the polymer with high



Fig. 2. WAXD patterns of polymers.



Fig. 3. DSC curves of polymers I-X.

viscosity was obtained for monomer concentration in the range of between 0.14 mol/L and 0.20 mol/L. A higher monomer concentration resulted in lower viscosity because the polymerization reaction was too fast and a gelatinous mass was formed after 4 h. However, a too low monomer concentration, for example, a monomer concentration of 0.10 mol/L, also gave a polymer with lower viscosity due to low rate of the polymerization reaction.

A series of novel poly(aryl ether ketone)s containing both diphenyl moiety and amide linkages in the main chains were synthesized by varying the molar ratio of BPOBDP to BPBPPD under the optimum polymerization reaction conditions. The polymerization results are summarized in Table 4. The inherent viscosity (η_{inh}) values of the polymers are above 0.79 dL/g and increased with the increase in concentration of BPBPPD in polymer due to the increase in strength of hydrogen bonding in the polymers. The inherent viscosity (η_{inh}) values reveal that high molecular weight polymers were obtained in DCE/NMP medium since the η_{inh} values of the polymers than the critical η_{inh} value of the macromolecule. Thus, the modified electrophilic Friedel–Crafts polycondensation route is appropriate.

The key structural features of the polymers obtained could be identified by FT-IR spectroscopy. The FT-IR spectra of all the

Table 5			
Thermal	properties	of the	polymers.

Polymer	$T_{\rm g}~(^{\circ}{\rm C})$	$T_{\rm m}$ (°C)	T_{c} (°C)	DT_5 (°C)	DT ₁₀ (°C)
I	207	368	297	488	517
II	202	362	291	500	521
III	195	346	286	508	533
IV	192	341	282	515	541
V	189	328	269	517	542
VI	185	314	268	521	545
VII	183	324	263	531	553
VIII	178	336	247	533	556
IX	175	351	229	535	563
Х	170	365	225	547	571



Fig. 4. TGA curve of the polymer V.

polymers show no absorption at about 1740 cm⁻¹ indicating the absence of –COCl groups. All the spectra of the polymers except for the polymer X without BPBPPD show characteristic bands at 3431 cm^{-1} due to N–H stretch, at 1655 cm^{-1} due to aromatic ketone and amide C=O stretch, at 1399 cm^{-1} due to amide C–N stretch and at 1239 cm^{-1} due to Ar–O–Ar stretch. The FT-IR spectrum of the polymer VI is shown in Fig. 1.

The crystallinities of the polymers were evaluated by wideangle X-ray diffraction (WAXD). All the polymers obtained exhibited semicrystalline patterns. The WAXD patterns of the polymers II, IV, VI, VIII and X are presented in Fig. 2. It is well documented that poly(aryl ether ketone ketone) with 100 mol% IPC (PEKmK) had three major diffraction peaks at 2θ that are 18.7° (110), 23.3° (200) and 28.9° (211) [13]. As shown in Fig. 2, the WAXD patterns of the polymers IV, VI, VIII and X with 30-100 mol% BPOBDP also had three major diffraction peaks at 2θ that are 18.8° (110), 22.9° (200) and 28.4° (211), which indicated that the polymers IV, VI, VIII and X had the chain similar to that of the PEKmK to form the crystal that was included in the orthorhombic system with the PEKmK. The polymer II with 90 mol% BPBPPD showed only an intensive diffraction peak at $2\theta \sim 20.2^\circ$, which did not indicate clearly that the polymer II was a semicrystalline. However, from the DSC analysis of the polymer II. we can see that the crystallization exothermic peak was observed from the DSC curve of the polymer II (Fig. 3). The DSC analysis results further indicated that polymers IV, VI, VIII, and X were semicrystalline.

3.4. Properties of polymers

The thermal properties of the polymers were evaluated by DSC and TGA and the results are given in Table 5. Samples were heated up to 400 °C at the rate of 10 °C min⁻¹ in N₂, quenched to -50 °C and rerun to obtain T_{g} . The T_{g} s of the polymers I–X were 170–207 °C, which exhibited much higher T_{g} s than those of commercially available PEEK and PEKK, Tgs of which were 143 and 156 °C, respectively. This attributed to the presence of hydrogen bonding and diphenyl moieties in the polymers. The T_{g} values of the polymers I-X increased with the increase in concentration of BPBPPD in the polymer, the polymer I with 100 mol% BPBPPD had the highest $T_{\rm g}$ of 207 °C, 37 °C higher than that of the polymer X with 100 mol% BPOBDP, which indicated that the amide linkages due to the formation of hydrogen bonding are more effective than diphenyl moieties due to the rigidity for the improvement of T_{g} . The increased Tg values of the polymers I-IX can be explained by the fact that the intermolecular interaction force was enhanced and the segmental motion was hindered due to the presence of

Table 6 Solubility of the polymers.^a

Polymer	H_2SO_4	NMP	DMAc	DMSO	DMF	THF	CHCl ₃	DCE	EtOH
Ι	+	+-	_	+-	_	_	_	_	_
II	+	+-	_	+-	_	_	_	_	_
III	+	+-	_	+-	_	_	_	_	_
IV	+	+-	_	+-	_	_	_	_	_
V	+	+-	_	_	_	_	_	_	_
VI	+	+-	_	_	_	_	_	_	_
VII	+	_	_	_	_	_	_	_	_
VIII	+	_	_	_	_	_	_	_	_
IX	+	_	_	_	_	_	_	_	_
Х	+	-	-	-	-	-	-	-	-

+: soluble, +-: swollen, -: insoluble.

^a The solubility was tested at a concentration of 10 mg/mL in the solvent at room temperature for 24 h.

intermolecular hydrogen bonding of amide groups. The crystalline temperatures (T_cs) of the polymers I–X were 225–297 °C and also increased with the increase in concentration of BPBPPD in the polymer. The $T_{\rm m}$ s of the polymers I–X were 314–368 °C and the polymer I with 100 mol% BPBPPD had the highest T_m of 368 °C. The $T_{\rm m}$ values of the polymers I–VI decreased gradually with the increase in concentration of BPOBDP in the polymer because the strengths of hydrogen bonding between the molecular chains were diminished by the addition of BPOBDP. When the molar ratio of BPOBDP to BPBPPD was 50/50, the resulting polymer VI had the lowest $T_{\rm m}$ of 314 °C. Then, the $T_{\rm m}$ values of the polymers VI–X increased gradually with the increase in concentration of BPOBDP in the polymer due to the increase in the rigidity of the molecular mains, the polymer X with 100 mol% BPOBDP had high $T_{\rm m}$ of 365 °C. The wholly para-linked poly(aryl ether ketone ketone) (p-PEKK) also had a high T_g of 170 °C, but its too high T_m of 384 °C made it unsuitable for the melt processing. However, the polymers V-VII with 40-60 mol% BPBPPD had not only high T_gs of 183-189 °C, but also moderate T_ms of 314–328 °C, having good potential for the melt processing. The DSC curves of the polymers are illustrated in Fig. 3.

Poly(aryl ether ketone)s containing both diphenyl moiety and amide linkages in the main chains exhibited high thermal stability. As summarized in Table 5, the temperatures at 5% weight loss (DT₅) are above 488 °C and the temperatures at 10% weight loss (DT₁₀) are above 517 °C in nitrogen. The DT₅ and DT₁₀ values of the polymers decreased with the increase in BPBPPD content in polymer since poly(aryl ether ketone)s had higher DT₅ and DT₁₀ values than aromatic polyamides. The Polymer I with 100 mol% BPBPPD had the lowest DT₅ (488 °C) and DT₁₀ (517 °C) values, while polymer X without BPBPPD had the highest DT₅ (547 °C) and DT₁₀ (571 °C) values. The temperature difference between $T_{\rm m}$ and DT₅ of the polymers V–VII was large, thus the melt processing could be easily accomplished. The typical TGA curve of the polymer V is illustrated in Fig. 4.

The solubility behavior of the polymers prepared in this study was examined for powdery samples at a concentration of 10 mg/mL in the solvents at room temperature for 24 h and the results are

Table 7				
Mechanical	properties	of the	polymers	IV-VIII.

Polymer	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)
IV	112.8	2.64	9.7
V	111.5	2.45	11.3
VI	110.2	2.31	12.6
VII	107.4	2.20	13.5
VIII	104.1	2.36	12.9



Fig. 5. Stress-strain curves of the polymer VI.

listed in Table 6. All the polymers were insoluble in highly polar solvents such as NMP, DMAc, DMSO, and DMF except for concentrated sulfuric acid. However, the polymers I–IV with 70–100 mol% BPBPPD can be swelled in NMP and DMSO. The polymers I–X were also insoluble in common organic solvents such as THF, CHCl₃, DCE, EtOH, acetone, toluene and so on. Thus, from the results above, we conclude that semicrystalline polymers I–X have good resistance to organic solvents.

The mechanical properties of the polymers IV–VIII are presented in Table 7. From these data, it can be seen that the polymers IV–VIII had tensile strengths of 104.1–112.8 MPa, Young's moduli of 2.20– 2.64 GPa, and elongations at break of 9.7–13.5%, indicating that they are strong materials. The representative stress–strain curves of the polymer VI are presented in Fig. 5.

4. Conclusion

In summary, novel poly(aryl ether ketone)s containing both diphenyl moiety and amide linkages in the main chains were successfully synthesized by electrophilic Friedel-Crafts solution copolycondensation of IPC with a mixture of BPOBDP and BPBPPD, over a wide range of BPOBDP/BPBPPD molar ratios, under very mild conditions. All the polymers are semicrystalline and the polymers I–X had remarkably increased T_os of 170–207 °C over commercially available PEEK (143 °C) and PEKK (156 °C) due to the incorporation of the diphenyl moiety and amide linkages in the main chains. The $T_{\rm m}$ s of the polymers I–X were 314–368 °C and the polymer VI with 50 mol% BPBPPD had the lowest T_m of 314 °C. The polymers V–VII with 40–60 mol% BPBPPD had not only high T_gs of 183–189 °C, but also moderate $T_{\rm m}$ s of 314–328 °C, having good potential 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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