# Synthesis and Characterization of Poly(ether amide ether ketone)/Poly(ether ketone ketone) Copolymers

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**ABSTRACT:** A new monomer, $N,N'$-bis(4-phenoxybenzoyl)-$m$-phenylenediamine (BPPD), was prepared by condensation of $m$-phenylenediamine with 4-phenoxybenzoyl chloride in $N,N$-dimethylacetamide (DMAc). A series of novel poly(ether amide ether ketone) (PEAEK)/poly(ether ketone ketone) (PEKK) copolymers were synthesized by the electrophilic Friedel-Crafts solution copolycondensation of terephthaloyl chloride (TPC) with a mixture of diphenyl ether (DPE) and BPPD, over a wide range of DPE/BPPD molar ratios, in the presence of anhydrous $AlCl_3$ and $N$-methylpyrrolidone (NMP) in 1,2-dichloroethane (DCE). The influence of reaction conditions on the preparation of copolymers was examined. The copolymers obtained were characterized by different physicochemical techniques. The copolymers with 10–25 mol % BPPD were semicrystalline and had remarkably increased $T_g$s over commercially available PEEK and PEKK due to the incorporation of amide linkages in the main chains. The copolymers III and IV with 20–25 mol % BPPD had not only high $T_g$s of 184–188°C, but also moderate $T_m$s of 323–344°C, having good potential for the melt processing. The copolymers III and IV had tensile strengths of 103.7–105.3 MPa, Young's moduli of 3.04–3.11 GPa, and elongations at break of 8–9% and exhibited outstanding thermal stability and good resistance to organic solvents. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 647–653, 2011

**Key words:** poly(ether ketone); poly(ether amide ether ketone); electrophilic solution polycondensation; terephthaloyl chloride; thermal property

## INTRODUCTION

Aromatic poly(ether ketone)s (PEKs) are a family of semicrystalline, insoluble, high-temperature, high-performance engineering thermoplastics.[1-3] They display an excellent combination of physical, thermal, and mechanical properties and solvent-resistance characteristics and are used in aerospace, electronics, and nuclear fields.[4-8] There are two general synthetic pathways to produce PAEKs.[9,10] 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 route has been the popular method to prepare various kinds of aromatic poly(ether ketone)s because the polymerization reaction conditions are mild and the monomers, which are used in the electrophilic approach, have been more selective, cheaper, and readily available.[11-16] Drawbacks of aromatic poly(ether ketone)s include their high cost, high processing temperatures, and relatively low glass transition temperatures. In advanced composite applications it is desirable to utilize PEK materials with high-glass transition temperatures.

The wholly *para*-linked poly(ether ketone ketone)($p$-PEKK) has made it difficult to process due to its high melting point of 384°C. The very poor flowing property and the too high processing temperature (over 430°C) for the $p$-PEKK was even difficult for the processing capacity of the ZSK 30P 9P Lab extruding machine (from Germany). To improve its glass transition temperature and processability, some modifications were made on the $p$-PEKK.[17,18] The incorporation of low levels of 1,3-connected *meta*-phenylene linkages into the all-*para* backbone of PEKK has been shown to produce a substantial reduction in equilibrium melting temperature and a modest decrease in glass transition temperature,[13] this latter effect is attributed to an increase in overall chain flexibility with the introduction of the *meta* linkages. Recently, we synthesized a new monomer, $N,N'$-bis(4-phenoxybenzoyl)-$m$-phenylenediamine (BPPD), via simple synthetic procedures from readily available materials. Considering the fact that the BPPD contains both amide and 1,3-connected *meta*- phenylene linkages, we expected that the semicrystalline

copolymers with high $T_g$s and moderate $T_m$s could be obtained by the incorporation of lower contents of BPPD into the all-*para* backbone of the *p*-PEKK due to the presence of hydrogen bonding and 1,3-connected *meta*-phenylene linkages in the polymers. In this article, we synthesized the copolymers of poly(ether amide ether ketone) (PEAEK) and poly(ether ketone ketone) (PEKK) by the electrophilic Friedel-Crafts solution copolycondensation of terephthaloyl chloride (TPC) with a mixture of diphenyl ether (DPE) and BPPD, over a wide range of DPE/BPPD molar ratios, in the presence of anhydrous aluminum chloride and *N*-methylpyrrolidone (NMP) in 1,2-dichloroethane (DCE). The copolymers were characterized by FTIR, wide-angle X-ray diffraction (WAXD), differential scanning calorimeter (DSC), and thermal gravimetric analysis (TGA). The results indicated that the copolymers have a potentiality for industry.

## EXPERIMENTAL

### Materials

All reagents and solvents were of analytical grade and were used without further purification unless stated otherwise. Terephthaloyl chloride (TPC, Shuanglin Chemical, Nanchang, China) was purified by distillation under vacuum before use. 1,2-Dichloroethane (DCE, Shanghai Chemical Reagent, Shanghai, China), *N*-methylpyrrolidone (NMP, Shanghai Chemical Reagent), *N,N*-dimethylacetamide (DMAc, Shanghai Chemical Reagent), diphenyl ether (DPE, 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 before use. *m*-Phenylenediamine (Shanghai Chemical Reagent) and *p*-phenoxybenzoic acid (Shanghai Chemical Reagent) were used as received.

### Synthesis

#### Preparation of BPPD

*N,N′*-Bis(4-phenoxybenzoyl)-*m*-phenylenediamine (BPPD) was synthesized by the condensation reaction of *m*-phenylenediamine with 4-phenoxybenzoyl chloride in *N,N*-dimethylacetamide (DMAc) as shown in Scheme 1.

To a 250 mL, round-bottomed flask was added 14.98 g (0.07 mol) of 4-phenoxy-benzoic acid, 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 3.24 g (0.03 mol) of *m*-phenylenediamine was added
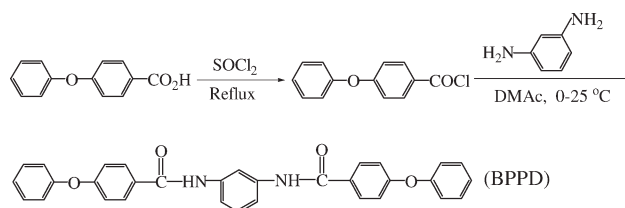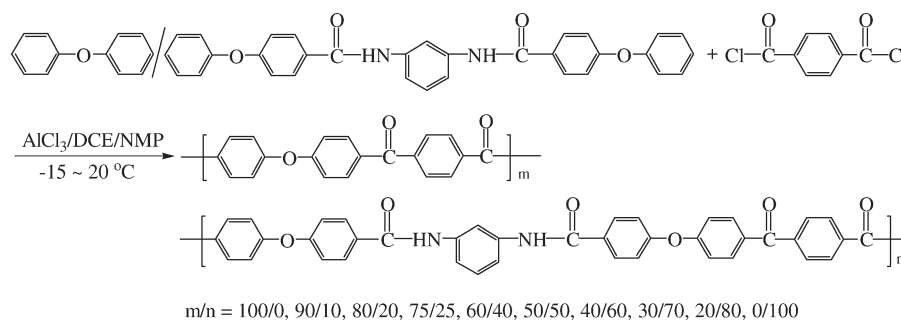
**Scheme 1** Preparation of BPPD.

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 ($V_{DMF}/V_{EtOH} = 1/2$) and dried under vacuum at 100°C to afford 12.06 g of white crystals. Yield 80%; m.p. 225–226°C; FTIR (KBr): ν = 3335, 1642, 1590, 1538, 1496, 1408, 1248, 846 cm$^{-1}$; $^{1}$H-NMR (DMSO-d$_6$): 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); $^{13}$C-NMR (DMSO-d$_6$): 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; MS (EI): *m/z* (%) = 500 (M$^+$, 30), 197 (100); Elemental analysis: calculated for C$_{32}$H$_{24}$N$_2$O$_4$; C, 76.79; H, 4.83; N, 5.59; Found: C, 76.60; H, 4.96; N, 5.44.

#### Polymerization

PEAEK/PEKK copolymers were prepared as shown in Scheme 2 by the electrophilic Friedel-Crafts solution copolycondensation of TPC with a mixture of DPE and BPPD, in the presence of anhydrous aluminum chloride and NMP in DCE. A typical preparative procedure for polymer VI is described as follows.

A total of 5.874 g (44 mmol) of anhydrous AlCl₃ and 15 mL of DCE was added to a 100-mL, three-necked, round-bottomed flask equipped with a mechanical stirrer, a thermometer, nitrogen inlet and outlet tubes. The flask was cooled to 0°C using an ice-water bath, then a solution of 2 mL (21 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 1.250 g (2.5 mmol) of BPPD, 0.425 g (2.5 mmol) of DPE, 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 0.1 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

m/n = 100/0, 90/10, 80/20, 75/25, 60/40, 50/50, 40/60, 30/70, 20/80, 0/100

**Scheme 2** Preparation of copolymers.

heated at 100°C overnight under vacuum to give the polymer VI. The aluminum content of the polymer VI was determined to be 7 ppm by ICP. Other polymers were also obtained by varying the molar ratio of DPE to BPPD in a similar manner.

## Measurements

Elemental analysis was performed with Perkin-Elmer Model 2400 CHN analyzer. The FTIR spectra of the monomers and polymers in KBr pellets (2%) were recorded using a Nicolet FTIR (510P) spectrophotometer. $^1$H-NMR (400 MHz) and $^{13}$C-NMR (100 MHz) spectra were obtained with a Bruker PC-A400 (400 MHz) spectrometer at an operating temperature of 25°C using DMSO-$d_6$ 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% $H_2SO_4$ 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 50 mm/min. The samples having dimensions of $4.0 \times 6.0 \times 55$ mm$^3$ were cut from the 55-mm$^2$ molding. 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 Cu Kα radiation, at 30 KV and 20 mA. The diffractograms were recorded at room temperature over the range of 10–40°. Samples were powder.

## RESULTS AND DISCUSSION

As shown in Scheme 1, the new monomer containing amide linkages, $N,N'$-bis(4- phenoxybenzoyl)-$m$-

phenylenediamine (BPPD), was conveniently prepared by the condensation reaction of $m$-phenylenediamine with 4-phenoxybenzoyl chloride in DMAc at 0–25 °C and could be obtained as a pure material after recrystallization from DMF/EtOH. FTIR, NMR, MS spectroscopies, and elemental analysis were used to confirm the structure of BPPD. In the IR spectrum, the key structural features include the following absorptions: N—H stretch, 3335 cm$^{-1}$, amide C=O stretch, 1642 cm$^{-1}$, amide C—N stretch, 1408 cm$^{-1}$, and Ar—O—Ar stretch, 1248 cm$^{-1}$. The $^1$H-NMR and $^{13}$C-NMR spectra of BPPD were in accordance with the proposed structure. The mass spectrum had a base peak at 197, which was due to phenoxybenzoyl cation.

A series of novel poly(ether amide ether ketone)(-PEAEK)/poly(ether ketone ketone) (PEKK) copolymers were prepared by the electrophilic Friedel-Crafts solution copolycondensation of terephthaloyl chloride (TPC) with a mixture of DPE and BPPD, over a wide range of DPE/BPPD molar ratios, as shown in Scheme 2. 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. Janson et al.[19] 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 aromatic poly(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

**TABLE I**
**Effect of AlCl3 Quantity on Polymerization[a]**

| AlCl$_3$ (molar ratio to TPC) | Yield (%) | $\eta_{inh}$[b] (dL/g) |
|:---:|:---:|:---:|
| 7.2 | 89 | 0.18 |
| 7.6 | 92 | 0.36 |
| 8.2 | 94 | 0.79 |
| 8.8 | 94 | 0.93 |
| 9.2 | 95 | 0.88 |
| 10.0 | 94 | 0.72 |

[a] Polymerized at 20°C with 2.5 mmol of DPE, 2.5 mmol of BPPD, 5 mmol of TPC, and 21 mmol of NMP in 25 mL of DCE for 20 h.
[b] Measured with a concentration of 0.2 g/dL in 95% sulfuric acid at 25°C.

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 (AlCl$_3$)/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 reaction mixture is more tractable, making work up of the polymer easier and ensuring effective removal of catalyst residues during purification. The solublization property of the Lewis acid (AlCl$_3$)/Lewis base complex is particularly significant in the preparation of *para*-linked aromatic poly (ether ketone)s.

Initially, to determine the optimum polymerization reaction conditions, the influences of catalyst quantity, Lewis base quantity and monomer concentration on the preparation of the copolymers were examined by Friedel-Crafts acylation of TPC with a mixture of 50 mol % DPE and 50 mol % BPPD in 1,2-dichloroethane using anhydrous aluminum chloride as a catalyst and NMP as a Lewis base. The preparation of PEKs by electrophilic Friedel-Crafts acylation polycondensation generally starts at low temperature. The initial low temperature is needed to maintain control over the reaction rate. A reaction temperature of about –15°C to –5°C has been found to be particularly effective. Thereafter, the reaction temperature is slowly increased and maintained 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 AlCl$_3$, and thereby deactivate it, AlCl$_3$ is generally employed at more than one equivalent of carbonyl groups in the reaction medium.[20,21] The optimum ratio of AlCl$_3$ to carbonyl group was reported to be 1.35–1.45.[11,22] In our modified Friedel-Crafts

acylation polycondensation, an additional amount of AlCl$_3$ was needed for the formation of a 1 : 1 complex of AlCl$_3$ and NMP due to the addition of Lewis base (NMP) as the controlling agent. Table I shows the effect of the AlCl$_3$/TPC feed ratio on the inherent viscosity of the polymer obtained. The polymerization reaction with 7.2 equivalents of AlCl$_3$ to TPC afforded a polymer with a low inherent viscosity of 0.18 dL/g due to the absence of a catalytic amount of AlCl$_3$. At least a molar equivalent excess of AlCl$_3$ 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 AlCl$_3$. When the molar ratio of AlCl$_3$ to TPC was in the range of between 8.2 and 9.2, a polymer with high inherent viscosity (>0.79 dL/g) could be obtained. However, a large excess of AlCl$_3$, for example, a ten-fold excess, resulted in a decreased inherent viscosity of the polymer. Therefore, a suitable quantity of AlCl$_3$ was about nine molar equivalents relative to TPC.

The effect of Lewis base (NMP) quantity on polymerization was also investigated and the results are summarized in Table II. As shown in Table II, the precipitation polycondensation reaction without NMP afforded a polymer with a lower inherent viscosity of 0.36 dL/g. The inherent viscosity of the polymer increased with increase in molar ratios of NMP to TPC from 2.0 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 TPC.

The Friedel-Crafts acylation polymerization also showed a characteristic effect of monomer concentration on the inherent viscosity of polymers. Table III shows the influence of monomer concentration on

**TABLE II**
**Effect of NMP Quantity on Polymerization[a]**

| NMP (molar ratio to TPC) | Yield (%) | $\eta_{inh}$[b] (dL/g) |
|:---:|:---:|:---:|
| 0 | 92 | 0.36 |
| 2.0 | 94 | 0.61 |
| 3.0 | 94 | 0.73 |
| 3.6 | 94 | 0.85 |
| 4.2 | 94 | 0.93 |
| 4.8 | 94 | 0.88 |
| 5.4 | 94 | 0.70 |

[a] Polymerized at 20°C with 2.5 mmol of DPE, 2.5 mmol of BPPD, 5 mmol of TPC, and 23 mmol of AlCl$_3$ in 25 mL of DCE for 20 h. In addition, one molar equivalent of AlCl$_3$ relative to NMP was required to form a 1 : 1 complex of AlCl$_3$ and NMP.
[b] Measured with a concentration of 0.2 g/dL in 95% sulfuric acid at 25 °C.

### TABLE III
### Effect of Monomer Concentration on polymerization[a]

| Monomer concentration (mol/L) | Yield (%) | $\eta_{inh}$[b] (dL/g) |
|---|---|---|
| 0.33 | 94 | 0.61 |
| 0.25 | 94 | 0.84 |
| 0.20 | 94 | 0.93 |
| 0.18 | 94 | 0.87 |
| 0.16 | 94 | 0.79 |
| 0.12 | 94 | 0.59 |

[a] Polymerized at 20°C with 2.5 mmol of DPE, 2.5 mmol of BPPD, 5 mmol of TPC, 21 mmol of NMP, and 44 mmol of $AlCl_3$ for 20 h.
[b] Measured with a concentration of 0.2 g/dL in 95% sulfuric acid at 25 °C.

### TABLE IV
### Polymerization Results[a]

| Polymer | DPE (mol %) | BPBMPD (mol %) | Yield (%) | $\eta_{inh}$[b] (dL/g) |
|---|---|---|---|---|
| I | 100 | 0 | 94 | 0.72 |
| II | 90 | 10 | 95 | 0.74 |
| III | 80 | 20 | 94 | 0.78 |
| IV | 75 | 25 | 94 | 0.85 |
| V | 60 | 40 | 94 | 0.90 |
| VI | 50 | 50 | 94 | 0.93 |
| VII | 40 | 60 | 95 | 0.97 |
| VIII | 30 | 70 | 94 | 1.02 |
| IX | 20 | 80 | 94 | 1.09 |
| X | 0 | 100 | 95 | 1.18 |

[a] Polymerized at 20°C with 5 mmol of TPC and 5 mmol of (DPE + BPPD) in 25 mL of DCE for 20 h.
[b] Measured with a concentration of 0.2 g/dL in 95% sulfuric acid at 25°C.

the polymer viscosity in the course of preparation of the PEAEK/PEKK copolymers. As shown in Table III, the polymer with high viscosity was obtained for monomer concentration in the range of between 0.18 mol/L and 0.25 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 0.12 mol/L, also gave a polymer with lower viscosity due to low rate of the polymerization reaction.

A series of novel PEAEK/PEKK copolymers were synthesized by varying the molar ratio of DPE to BPPD under the optimum polymerization reaction conditions. The polymerization results are summarized in Table IV. The inherent viscosity ($\eta_{inh}$) values of the polymers are above 0.72 dL/g and increased with the increase in concentration of BPPD in the polymer due to the increase in strength of hydrogen bonding in the polymers. The inherent viscosity ($\eta_{inh}$) values reveal that high molecular weight polymers were obtained in DCE/NMP medium since the $\eta_{inh}$ values of the polymers were higher than the critical $\eta_{inh}$ 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 FTIR spectroscopy. The FTIR spectra of all 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 I without BPPD show characteristic bands at 3431 cm$^{-1}$ due to N—H stretch, at 1657 cm$^{-1}$ due to aromatic ketone and amide C=O stretch, at 1417 cm$^{-1}$ due to amide C—N stretch and at 1240 cm$^{-1}$ due to Ar—O—Ar stretch. The FTIR spectrum of the copolymer VI is shown in Figure 1.

The crystallinities of the copolymers were evaluated by wide-angle X-ray diffraction (WAXD). The WAXD patterns of the copolymers II, III, IV, V, and

VIII are presented in Figure 2. It is well documented that the polymer I with 100 mol % DPE (p-PEKK) had four major diffraction peaks at 2θ that are 15.8° (020), 18.7° (110), 23.3° (200), and 28.9° (211).[13] As shown in Figure 2, the WAXD patterns of the copolymers II, III, and IV with 75–90 mol % DPE fundamentally bore the same number and site of diffraction peak of every crystal face crystal plane in comparison with that of the p-PEKK, but the diffraction peaks decreased in intensity with the increase in BPPD content due to the presence of 1,3-connected meta-phenylene linkages, which disrupted the regularity of molecular chains and inhibited the close packing of the polymer chains. When the molar ratio of BPPD to DPE was up to 40/60, the obtained copolymer V was amorphous and only showed a diffuse diffraction peak. The copolymer VIII with 70 mol % BPPD also exhibited amorphous pattern. The aforementioned results indicated that the copolymers II, III, and IV had the chain similar to that of the p-PEKK to form the crystal that was included in the orthorhombic system with the p-PEKK.

The thermal properties of the polymers were evaluated by DSC and TGA and the results are given in Table V. Samples were heated up to 400°C at the
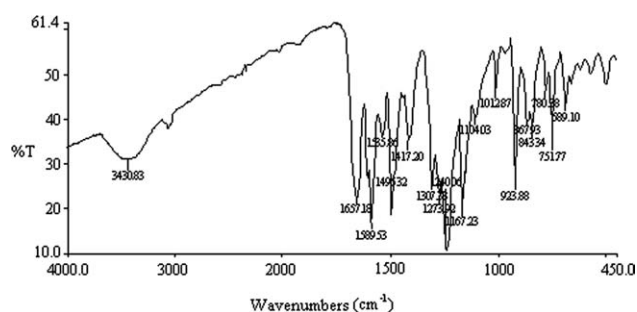


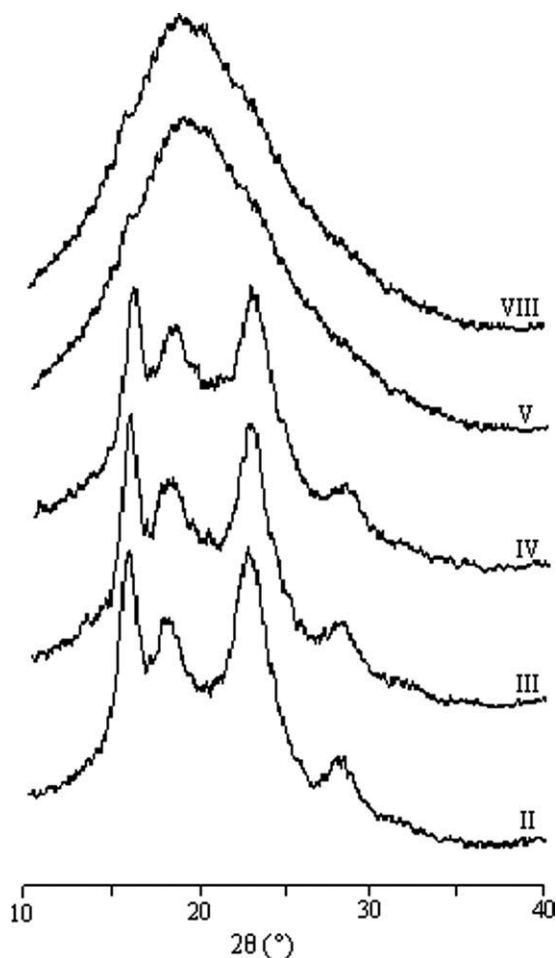**Figure 1** FTIR spectrum of the copolymer VI.

**Figure 2** The WAXD patterns of the copolymers II, III, IV, V, and VIII.

**TABLE V**
**Thermal Properties of the Polymers**

| Polymer | $T_g(°C)$ | $T_m(°C)$ | $T_c(°C)$ | $T_d(°C)$ |
|---------|-----------|-----------|-----------|-----------|
| I | 170 | 384 | 195 | 559 |
| II | 178 | 362 | 221 | 557 |
| III | 184 | 344 | 255 | 543 |
| IV | 188 | 323 | 271 | 525 |
| V | 204 | | | 509 |
| VI | 220 | | | 497 |
| VII | 229 | | | 488 |
| VIII | 233 | | | 485 |
| IX | 236 | | | 483 |
| X | 231 | | | 480 |

observed from DSC curve of the resulting polymer V. The polymers VI–X with 50–100 mol % BPPD also showed only a glass transition endothermic peak in their DSC curves. The above results agreed with the WAXD results. The polymer I (*p*-PEKK) had a higher $T_g$ of 170°C, but its too high $T_m$ of 384°C made it unsuitable for the melt processing. However, the copolymers III and IV with 20–25 mol % BPPD had not only high $T_g$s of 184–188°C, but also moderate $T_m$s of 323–344°C, having good potential for the melt processing. A typical DSC curve of the copolymer III is illustrated in Figure 3.

The PEAEK/PEKK copolymers exhibited high-thermal stability. As shown in Table V, the temperatures at 5% weight loss ($T_d$) of all the polymers were above 480°C in $N_2$. The $T_d$ values of the polymers decreased with the increase in BPPD content in polymer since aromatic poly(ether ketone)s had higher $T_d$s than aromatic polyamides. The semicrystalline copolymers II–IV had high $T_d$s of 525–557°C. The temperature difference between $T_m$ and $T_d$ of copolymers III and IV was large, thus the melt processing could be easily accomplished. We had measured the mechanical properties of the copolymers III and IV and the results are presented in Table VI. The copolymers III and IV had tensile strengths of 103.7–105.3 MPa, Young's moduli of 3.04–3.11 GPa, and elongations at break of 8–9%, indicating that they are strong materials.
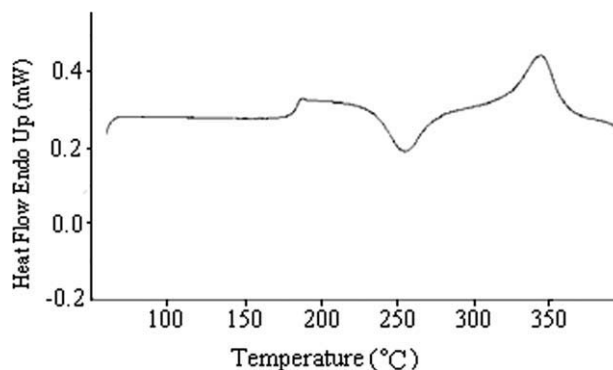
rate of 10°C/min in $N_2$, quenched to –50 °C and rerun to obtain $T_g$. The $T_g$s of the copolymers II–X were 178–236°C, which exhibited much higher $T_g$s than those of commercially available PEEK and PEKK, $T_g$s of which were 143 and 156°C, respectively. This attributed to the presence of hydrogen bonding in the polymers. The $T_g$ values of the polymers I–IX increased with the increase in concentration of BPPD in the polymer and the polymer I (*p*-PEKK) with 100 mol % DPE had the lowest $T_g$ of 170°C. The crystalline temperatures ($T_c$s) of the polymers I–IV were 195–271°C and also increased with the increase in concentration of BPPD in the polymer. The $T_m$'s of the polymers I–IV with 75–100 mol % DPE were 323–384°C and the polymer I (*p*-PEKK) with 100 mol % DPE had the highest $T_m$ of 384°C due to the high regularity of molecular chains. The $T_m$ values of the polymers I–IV decreased gradually with the increase in concentration of BPPD in the polymer due to the decrease in regularity of molecular chains with the introduction of the *meta*-phenylene linkages. When the molar ratio of BPPD to DPE was up to 40/60, no melting endothermic peak was

**Figure 3** DSC curve of the copolymer III.

**TABLE VI**
**Mechanical Properties of the Copolymers III and IV**

| Polymer | Tensile strength (MPa) | Young's Modulus (GPa) | Elongation at break (%) |
|---------|------------------------|------------------------|--------------------------|
| III | 105.3 | 3.04 | 9 |
| IV | 103.7 | 3.11 | 8 |

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. The polymer I (*p*-PEKK) had excellent resistance to organic solvents. The copolymers II–IX were insoluble in highly polar solvents such as NMP, DMAc, DMSO, and DMF except for concentrated sulfuric acid, but can be swelled in NMP and DMSO. The copolymers V–IX with 40–80 mol % BPPD can be swelled in all of the highly polar solvents. The polymer X with 100 mol % BPPD was soluble in NMP and DMAc due to the presence of 1,3-connected *meta*-phenylene linkages, which disrupted the regularity of molecular chains and led to increased free volume. The polymers II–X were also insoluble in common organic solvents such as THF, CHCl$_3$, DCE, EtOH, acetone, toluene, and so on. Thus, from the results above, we conclude that the semicrystalline copolymers II–IV had good resistance to organic solvents.

## CONCLUSIONS

1. High-molecular weight novel PEAEK/PEKK copolymers were conveniently synthesized by modified electrophilic Friedel-Crafts solution copolycondensation of terephthaloyl chloride (TPC) with a mixture of DPE and BPPD, over a wide-range of DPE/BPPD molar ratios, under very mild conditions.

2. The $T_g$ values of the copolymers increased with the increase in concentration of BPPD in the copolymer, while the $T_m$ values of the copolymers decreased and then disappeared with increasing BPPD content. The $T_m$(384°C) of the *p*-PEKK homopolymer can be reduced to 344°C when the molar ratio of BPPD/DPE was 20/80, moreover the glass transition temperature of the resulting copolymer III was 184°C, 14°C higher than that of the *p*-PEKK.

3. The copolymers III and IV with 20–25 mol % BPPD were semicrystalline and had not only high

$T_g$s of 184–188°C, but also moderate $T_m$s of 323–344 °C, having good potential for melt processing. The copolymers III and IV had tensile strengths of 103.7–105.3 MPa, Young's moduli of 3.04–3.11 GPa, and elongations at break of 8–9% and exhibited outstanding thermal stability and good resistance to organic solvents. These kinds of copolymers were thought to be promising high-performance engineering thermoplastic and advanced composite materials for use in aerospace, electronics, and nuclear fields.

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