Contents lists available at ScienceDirect

### **Reactive & Functional Polymers**

journal homepage: www.elsevier.com/locate/react

## REACTIVE & FUNCTIONAL POLYMERS

# 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

#### ARTICLE INFO

Article history: Received 13 September 2009 Received in revised form 25 November 2009 Accepted 29 November 2009 Available online 4 December 2009

Keywords: Poly(aryl ether ketone) Electrophilic solution polycondensation Terephthaloyl chloride Isophthaloyl chloride Thermal property

#### 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 (PEAAEKKs) 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<sub>g</sub>*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%.

© 2009 Elsevier Ltd. All rights reserved.

#### 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, thermooxidative, 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

E-mail address: 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



Abbreviations: BPBMPD, *N,N'*-bis(4-phenoxybenzoyl)-*m*-phenylenediamine; PEAAEKKs, 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).

<sup>\*</sup> Corresponding author. Fax: +86 791 8120388.

<sup>1381-5148/\$ -</sup> see front matter © 2009 Elsevier Ltd. All rights reserved. doi:10.1016/j.reactfunctpolym.2009.11.011

monomer containing amide linkages, *N*,*N'*-bis(4-phenoxybenzoyl)*m*-phenylenediamine (BPBMPD). Novel aromatic poly(ether amide amide ether ketone ketone)s (PEAAEKKs) 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<sup>+</sup>, 30), 197 (100). Elem. Anal.  $C_{32}H_{24}N_2O_4$  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>,  $\delta$ , ppm):  $\delta$  = 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>,  $\delta$ , ppm):  $\delta$  = 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 amide ether ketone ketone)s (PEAAEKKs) 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 diphenvl ether (DPE) as the end-capper for 1 h. guenched 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>,  $\delta$ , ppm):  $\delta$  = 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 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 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 CuKa



Scheme 1. Synthesis of BPBMPD.



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

Scheme 2. Synthesis of polymers.

radiation, at 30 kV and 20 mA. The diffractograms were recorded at room temperature over the range of  $10-40^{\circ}$ .

#### 3. Results and discussion

#### 3.1. Monomer synthesis

The route to the synthesis of a new monomer, *N*,*N*'-bis(4-phenoxybenzoyl)-*m*-phenylenediamine (BPBMPD), is shown in Scheme 1. The BPBMPD 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. FT-IR, NMR, MS spectroscopies and elemental analysis were used to confirm the structure of BPBMPD. In the IR spectrum, the key structural features include the following absorptions: N–H stretch, 3335 cm<sup>-1</sup>, amide C=O stretch, 1642 cm<sup>-1</sup>, amide C–N stretch, 1408 cm<sup>-1</sup>, and Ar–O–Ar stretch, 1248 cm<sup>-1</sup>. The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of BPBMPD were in accordance with the proposed structure.

#### 3.2. Polymer synthesis

Novel poly(ether amide amide ether ketone ketone)s (PEA-AEKKs) were prepared by electrophilic Friedel-Crafts solution copolycondensation of BPBMPD with a mixture of terephthaloyl chloride (TPC) and isophthaloyl chloride (IPC) 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 [22]. 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 [32]. Janson et al. [33] have reported that the Friedel-Crafts polymerization reaction can be controlled by the addition of a controlling agent to obtain the desired meltprocessable, 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 (AlCl<sub>3</sub>)/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 [33]. Furthermore, the 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 determine the optimum polymerization reaction conditions, the influences of catalyst quantity, Lewis base quantity and monomer concentration on the preparation of the PEAAEKKs were examined by Friedel-Crafts acylation of TPC with BPBMPD in 1,2-dichloroethane using anhydrous aluminum chloride as a catalyst and NMP as a Lewis base. The preparation of PAE-Ks 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  $-15 \degree$ C to  $-5 \degree$ 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. In general, Friedel-Crafts acylation gives a 1:1 complex of AlCl<sub>3</sub> and the carbonyl group formed. Therefore, an excess of AlCl<sub>3</sub> relative to the carbonyl group formed should be used to catalyze the reaction [34,35]. The optimum ratio of AlCl<sub>3</sub> to carbonyl group was reported to be 1.35-1.45 [19,36]. In our modified Friedel-Crafts acylation polycondensation, an additional amount of AlCl<sub>3</sub> was needed for the formation of a 1:1 complex of AlCl<sub>3</sub> and NMP

Table 1Effect of AlCl3 quantity on polymerization.<sup>a</sup>

AlCl <sub>3</sub> (molar ratio to TPC)	Yield (%)	$\eta_{inh}{}^{b}$ (dL/g)
7.6	91	0.21
8.0	91	0.43
8.4	92	0.75
8.8	94	1.07
9.2	94	1.32
9.6	94	1.21
10.0	94	0.98
10.4	93	0.84

 $^{\rm a}\,$  Polymerized at 20  $^{\circ}{\rm C}$  with 5 mmol of BPBMPD, 5 mmol of TPC, and 18 mmol of NMP in 30 mL DCE for 20 h.

 $^{\rm b}\,$  Measured with a concentration of 0.5 g/dL in NMP at 25 °C.

Table 2Effect of NMP quantity on polymerization.<sup>a</sup>

NMP (molar ratio to TPC)	Yield (%)	$\eta_{inh}^{b} (dL/g)$
0	92	0.44
2.0	93	0.73
2.6	94	0.97
3.2	94	1.22
3.6	94	1.32
4.0	95	1.19
5.0	94	0.88

<sup>a</sup> Polymerized at 20 °C with 5 mmol of BPBMPD, 5 mmol of TPC, and 28 mmol of AlCl<sub>3</sub> in 30 mL DCE for 20 h. In addition, one molar equivalent of AlCl<sub>3</sub> relative to NMP was required to form a 1:1 complex of AlCl<sub>3</sub> and NMP.

<sup>b</sup> Measured with a concentration of 0.5 g/dL in NMP at 25 °C.

#### Table 3

Effect of monomer concentration on polymerization.<sup>a</sup>

Monomer concentration (mol/L)	Yield (%)	$\eta_{inh}{}^{b}(dL/g)$
0.33	93	0.53
0.25	94	0.81
0.20	94	1.10
0.17	94	1.32
0.14	95	1.15
0.12	94	0.89
0.10	94	0.64

 $^a\,$  Polymerized at 20  $^\circ C$  with 5 mmol of BPBMPD, 5 mmol of TPC, 18 mmol of NMP, and 46 mmol of AlCl\_3 for 20 h.

Measured with a concentration of 0.5 g/dL in NMP at 25 °C.

#### Table 4

Polymerization results.<sup>a</sup>

Polymer	TPC (mol%)	IPC (mol%)	Yield (%)	$\eta_{inh}^{b}$ (dL/g)
I	100	0	94	1.32
II	90	10	95	1.19
III	80	20	94	1.29
IV	70	30	95	1.28
V	60	40	95	1.30
VI	50	50	95	1.36
VII	0	100	94	1.34

<sup>a</sup> Polymerized at 20 °C with 5 mmol of BPBMPD, 5 mmol of (TPC + IPC), 18 mmol of NMP, and 46 mmol of  $AlCl_3$  in 30 mL of DCE for 20 h.

<sup>b</sup> Measured with a concentration of 0.5 g/dL in NMP at 25 °C.

due to the addition of Lewis base (NMP) as the controlling agent. Table 1 shows the effect of the AlCl<sub>3</sub>/TPC feed ratio on the inherent viscosity of the polymer obtained. The polymerization reaction with 7.6 equivalents of AlCl<sub>3</sub> to TPC afforded a polymer with a low inherent viscosity of 0.21 dLg<sup>-1</sup> due to the absence of a catalytic amount of AlCl<sub>3</sub>. At least a molar equivalent excess of AlCl<sub>3</sub> 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<sub>3</sub>. When the molar ratio of AlCl<sub>3</sub> to TPC was in the range of between 8.8 and 9.6, a polymer with high inherent viscosity (>1.07 dL/g) could be obtained. However, a large excess of AlCl<sub>3</sub>, for example, a 10-fold excess, resulted in a decreased inherent viscosity of the polymer. Therefore, a suitable quantity of AlCl<sub>3</sub> was about 9.2 M equivalents relative to TPC.

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 0.44 dL  $g^{-1}$ . The inherent viscosity of the polymer increased with increase in molar ratios of NMP to TPC from 2.0 to 3.6 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 3.6 M equivalents relative to TPC.

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 PEAAEKKs. As shown in Table 3, the polymer with high 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 3 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 PEAAEKKs were synthesized by varying the molar ratio of TPC to IPC under the optimum polymerization reaction conditions. The polymerization results are summarized in Table 4. The inherent viscosity ( $\eta_{inh}$ ) values of the polymers are above 1.19 dL/g, which reveals that high molecular weight polymers were obtained in DCE/NMP medium. Thus, the modified electrophilic Friedel–Crafts polycondensation route is appropriate.

The chain structure of the polymers obtained was confirmed by FT-IR and NMR spectroscopy. The FT-IR spectra of all polymers show no absorption at about  $1740 \text{ cm}^{-1}$  indicating the absence of –COCl groups. All the spectra show the characteristic absorption



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



Fig. 2. <sup>1</sup>H NMR spectrum of the polymer I (DMSO-*d*<sub>6</sub>, 400 MHz).

bands around  $3429 \text{ cm}^{-1}$  due to N–H stretch, around  $1656 \text{ cm}^{-1}$  due to aromatic ketone and amide C=O stretch, around  $1419 \text{ cm}^{-1}$  due to amide C–N stretch and around  $1240 \text{ cm}^{-1}$  due to Ar–O–Ar stretch. The FT-IR spectrum of the polymer V is shown in Fig. 1. <sup>1</sup>H NMR spectrum of the polymer I is illustrated in Fig. 2, which agreed with the proposed polymer structure, indicating that side reactions such as ortho substitution of activated aryloxy groups and alkylation of the polymer did not occur during the modified Friedel–Crafts acylation polycondensation.

The crystallinities of the polymers were evaluated by wide-angle X-ray diffraction (WAXD). All the polymers exhibited amorphous patterns. The amorphous behavior of the polymers was due to the existence of 1,3-dibenzoylaminobenzene moieties in the main chain. The WAXD patterns of polymers I, IV, and VII are presented in Fig. 3.



Fig. 3. WAXD patterns of the polymers I, IV and VII.

#### 3.3. Thermal properties of PEAAEKKs

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<sup>-1</sup> in N<sub>2</sub>, quenched to -50 °C and rerun to obtain  $T_g$ . The  $T_g$ s of the polymers I–VII were 220–231 °C, which exhibited much higher  $T_g$ s than those of commercially available PEEK and PEKK,  $T_g$ s of which were 143 and

Table 5			
Thermal	properties	of the	polymers.

Polymer	<i>T<sub>g</sub></i> (°C)	DT <sub>5</sub> (°C)	DT <sub>10</sub> (°C)
I	231	480	521
II	229	483	527
III	227	486	528
IV	226	485	525
V	224	473	515
VI	223	477	516
VII	220	482	525



Fig. 4. DSC curves of the polymers (second heating, 10 °C/min).

Table 6		
Solubility	of the	polymers. <sup>a</sup>

Polymer	NMP	DMAc	DMF	DMSO	Acetone	THF	CHCl <sub>3</sub>	DCE	EtOH	Toluene
Ι	+	+	+	+	-	-	-	-	-	-
II	+	+	+	+	-	-	-	-	-	-
III	+	+	+	+	-	-	-	-	-	-
IV	+	+	+	+	-	-	-	-	-	-
V	+	+	+	+	-	-	-	-	-	-
VI	+	+	+	+	-	-	-	-	-	-
VII	+	+	+	+	-	-	-	-	-	-
III IV V VI VII	+ + + +	+ + + + +	+ + + +	+ + + +	- - - -	- - - -	- - - -	- - -	- - - -	- - - -

+: soluble, -: insoluble.

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

156 °C, respectively. This attributed to the presence of strong hydrogen bonding in the PEAAEKKs. The  $T_{g}s$  values of the polymers I–VII increased with increase in concentration of TPC in the polymer. The  $T_{g}s$  values of the polymers fall in a very narrow range since the high  $T_{g}s$  values of the polymers mainly result from the presence of strong hydrogen bonding in the PEAAEKKs and the influence of varying the ratio of TPC/IPC on the  $T_{g}s$  values of the polymers was minor. No melting endotherms were observed in the DSC traces, which further confirmed the amorphous nature of the polymers. The DSC curves of the polymers are illustrated in Fig. 4. The PEAAEKKs exhibited good thermal stability. As summarized in Table 5, The temperatures at 5% weight loss (TD<sub>5</sub>) of the polymers were above 473 °C and the temperatures at 10% weight loss (TD<sub>10</sub>) were above 515 °C in nitrogen.

#### 3.4. Solubility and mechanical properties of PEAAEKKs

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 listed in Table 6. All the polymers prepared were soluble in aprotic polar solvents such as NMP, DMAc, DMSO, and DMF. The good solubility of these polymers could be attributed to the presence of 1,3-dibenzoylaminobenzene moieties in the main chain, which disturb the close packing of the polymer chains and lead to the increasing free volume. However, all the polymers were insoluble in common organic solvents such as THF, CHCl<sub>3</sub>, DCE, EtOH, acetone, toluene and so on.

The mechanical properties of the polymer thin films cast from NMP are presented in Table 7. All the films were transparent, strong, and flexible. The polymer films had 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%, indicating that they are strong materials. The obtained amorphous copolymers had high mechanical strength with tensile strength above 100 MPa, higher than the semi-crystalline commercial PEEK (90–100 MPa) because the intermolecular interaction force of the polymers was enhanced due to the presence of intermolecular hydrogen bonding of amide groups, compared with PEEK without amide groups. All the polymers had high inherent viscosity ( $\eta_{inh}$ ) values of 1.19–1.36 dL/g

Tal	ble	7
-----	-----	---

Mechanical properties of the polymers.

Polymer	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)
I	105.8	2.86	9.8
II	108.2	2.70	11.2
III	104.7	2.69	10.8
IV	106.1	2.53	11.9
V	108.5	2.75	10.3
VI	107.3	2.62	12.6
VII	102.9	2.44	13.7

and similar macromolecular chain structures, which may explain the fact that tensile strengths and elongations at break of the polymers I–VII fall in a very narrow range.

#### 4. Conclusions

Novel aromatic poly(ether amide amide ether ketone ketone)s (PEAAEKKs) were conveniently synthesized by the modified electrophilic Friedel–Crafts solution copolycondensation of BPBMPD with a mixture of terephthaloyl chloride (TPC) and isophthaloyl chloride (IPC) under mild conditions. All the polymers were amorphous and had remarkably improved solubility in aprotic polar solvents such as NMP, DMAc, DMSO, and DMF. These 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%. Therefore, these polymers may be potential candidates for high-temperature optical materials and gas-separation membranes.

#### Acknowledgements

We thank the National Natural Science Foundation of China (Project 20764001) and Science Foundation of Department of Education of Jiangxi Province for financial support.

#### References

- [1] J.B. Rose, Polymer 15 (1974) 456.
- [2] T.E. Attwood, P.C. Dawson, J.L. Freeman, L.R.J. Hoy, J.B. Rose, P.A. Staniland, Polymer 22 (1981) 1096.
- [3] X.L. Ji, D.H. Yu, W.J. Zhang, Z.W. Wu, Polymer 38 (1997) 3501.
- [4] H.X. Nguyen, H. Ishida, Polym. Compos. 8 (1987) 57.
- [5] S. Khan, J.F. Pratte, I.Y. Chang, W.H. Krueger, Int. SAMPE Symp. Exhib. 35 (1990) 1579.
- [6] M.F. Teasley, B.S. Hsiao, Macromolecules 29 (1996) 6432.
- [7] S.K. Park, S.Y. Kim, Macromolecules 31 (1998) 3385.
- [8] J.B. Baek, S.Y. Park, G.E. Price, C.B. Lyons, L.S. Tan, Polymer 46 (2005) 1543.
- [9] X. Yue, H. Zhang, W. Chen, Y. Wang, S. Zhang, G. Wang, Z. Jiang, Polymer 48 (2007) 4715.
- [10] R.J. Cotter, Engineering Plastics: A Handbook of Polyarylethers, Gordon and Breach Publishers, Basel, 1995.
- [11] P.A. Staniland, In Comprehensive Polymer Science, in: G. Allen (Ed.), 5, Pergamon Press, Oxford, 1989, p. 483.
- [12] J.B. Rose, In High Performance Polymers: Their Origin and Development, in: R.B. Seymour, G.S. Kirshenbaum (Eds.), Elsevier, New York, 1986, p. 187.
- [13] M.J. Mullins, E.P. Woo, J. Macromol. Sci., Rev. Macromol. Chem. Phys. C 27 (1987) 313.
- [14] K.P. Chan, Y. Wang, A.S. Hay, Macromolecules 28 (1995) 653.
- [15] R. Singh, A.S. Hay, Macromolecules 24 (1991) 2637.
- [16] A. Ben-Haida, H.M. Colquhoun, P. Hodge, D.J. Williams, Macromolecules 39 (2006) 6467.
- [17] J. Wang, Y. Gao, A.R. Hlil, A.S. Hay, Macromolecules 41 (2008) 298.
- [18] H.M. Colquhoun, P. Hodge, F.P.V. Paoloni, P. Terry McGrail, P. Cross, Macromolecules 42 (2009) 1955.
- [19] Y. Sakaguchi, M. Tokai, Y. Kato, Polymer 34 (1993) 1512.
- [20] M.G. Zolotukhin, M. Dosieret, C. Fougnies, D. Villers, N.G. Gileva, A.A. Fatykhov, Polymer 36 (1995) 3575.
- [21] R.K. Krishnaswamy, D.S. Kalika, Polymer 37 (1996) 1915.
- [22] M.G. Zolotukhin, D.R. Rueda, F.J. Balta Calleja, M.E. Cagiao, E.A. Sedova, N.G. Gileva, Polymer 38 (1997) 1471.

- [23] D.R. Rueda, M.G. Zolotukhin, M.E. Cagiao, F.J. Balta Calleja, D. Villers, M. Dosiere, Macromolecules 29 (1996) 7016.
- [24] M.G. Zolotukhin, H.M. Colquhoun, L.G. Sestiaa, D.R. Rueda, D. Flot, Macromolecules 36 (2003) 4766.
- [25] H.M. Colquhoun, L.G. Sestiaa, M.G. Zolotukhin, D.J. Williams, Macromolecules 33 (2000) 8907.
- [26] F. Wang, J. Roovers, P.M. Toporowski, Macromolecules 26 (1993) 3826.
- [27] G.S. Bennett, R.J. Farris, S.A. Thompson, Polymer 32 (1991) 1633.
- [28] F. Wang, J. Roovers, J. Polym. Sci., Part A: Polym. Chem. 32 (1994) 2413.
  [29] B. Liu, G. Wang, W. Hu, Y. Jin, C. Chen, Z. Jiang, W. Zhang, Z. Wu, Y. Wei, J. Polym. Sci., Part A: Polym. Chem. 40 (2002) 3392.
- [30] Y. Zhang, X. Sun, R. Xu, Y. Niu, G. Wang, Z. Jiang, Mater. Chem. Phys. 99 (2006) 465.
- [31] Y. Niu, X. Zhu, L. Liu, Y. Zhang, G. Wang, Z. Jiang, React. Funct. Polym. 66 (2006) 559.

- [32] W.H. Bonner, US Pat. 3065205, 1962.
  [33] V. Janson, H.C. Gors, WO 8403891, 1984.
  [34] G.A. Olah (Ed.), Friedel–Crafts and Related Reactions, 3, Interscience, New York, 1964, p. 1003.
- [35] L.K. Tan, S. Brownstein, J. Org. Chem. 47 (1982) 4737.
  [36] N.G. Gileva, M.G. Zolotukhin, S.N. Salazkin, V.S. Sultanova, H.-H. Hörhold, D. Raabe, Acta Polym. 39 (1988) 452.