

Synthesis and properties of novel poly(aryl ether ketone)s containing imide linkages in the main chains

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Abstract A new monomer containing imide linkages, bis[4-(*p*-phenoxybenzoyl)-1,2-benzenedioyl]-*N,N,N',N'*-4,4'-diaminodiphenyl ether (BPBDADPE), was prepared by the Friedel–Crafts reaction of bis(4-chloroformyl-1,2-benzenedioyl)-*N,N,N',N'*-4,4'-diaminodiphenyl ether (BCBDADPE) with diphenyl ether (DPE). Novel poly(aryl ether ketone)s containing imide linkages in the main chains (PEK-I) were synthesized by electrophilic Friedel–Crafts solution copolycondensation of terephthaloyl chloride (TPC) with a mixture of DPE and BPBDADPE. The polymers were characterized by different physico-chemical techniques. The polymers with 10–40 mol% BPBDADPE are semicrystalline and had increased T_g s over commercially available poly(ether ether ketone) (PEEK) and poly(ether ketone ketone) (PEKK) (70/30) due to the incorporation of imide linkages in the main chains. The polymers IV and V with 30–40 mol% BPBDADPE had not only high T_g s of 182–183 °C, but also moderate T_m s of 341–343 °C, having good potential for melt processing and exhibited high thermal stability and good resistance to common organic solvents.

Keywords Poly(aryl ether ketone) · Electrophilic solution polycondensation · Imide · Terephthaloyl chloride · Thermal property

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Introduction

Crystalline poly(aryl ether ketone)s (PAEKs) are a family of high-temperature engineering thermoplastics with an excellent combination of physical, thermal, and mechanical properties and solvent resistance characteristics. This class of advanced materials is currently receiving considerable attention for potential applications in aerospace, automobile, electronics, and other high technology fields [1–3]. The literature cites two main synthetic routes to PAEKs [4–6]: (1) the nucleophilic aromatic displacement of carbonyl-activated halides by phenoxide anions [7–11] and (2) the Friedel–Crafts electrophilic aromatic polyacylation condensation [12–17]. Normally, the preparation involving nucleophilic aromatic substitution is conducted at 300 °C and even higher temperatures. While each method has its own merits and drawbacks, the electrophilic route has usually been used to prepare various kinds of PAEKs 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. Drawbacks of PAEKs include their high cost, high processing temperatures, and relatively low glass transition temperatures. In advanced composite applications it is desirable to utilize PAEK materials with higher glass transition temperatures.

Modification of PAEK properties is desired for many applications. On the other hand, the synthesis and investigation of novel PAEKs would be very useful for a more rigorous structure–property correlation of this very interesting class of polymers. One effective method of varying polymer properties involves the incorporation of a variety of groups in the main chains. Among these, stiff and bulky group such as diphenyl or naphthalene is of considerable interest because it offers good advantages concerning the stability and thermal resistance of the resulting polymer. Considering the fact that PAEKs [e.g., poly(ether ether ketone) (PEEK)] suffer from poor creep behavior above their relatively low glass transitions, the synthesis of semicrystalline PAEKs with increased T_g is of high interest. For example, it is well-known that the incorporation of rigid and bulky groups in the main chain leads to an increase in the temperature of the glass transition. Some papers have reported the synthesis of novel PAEKs containing diphenyl or naphthalene moieties by the nucleophilic aromatic substitution polycondensation [18–23]. Zolotukhin et al. [13] reported the synthesis of naphthalene-containing polyketones by precipitation electrophilic polycondensation, the polymers obtained possess high T_g s values (>180 °C) and also too high T_m s values (>380 °C), which made it difficult to process. Shibata et al. reported the synthesis of the block copolymers of the PEEK and the poly(aryl ether sulfone) containing biphenylene moiety (PEBS) [24]. 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.

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 *p*-PEKK was even difficult for the processing capacity of the ZSK 30P 9P Lab extruding machine (from Germany). 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 [14], this latter effect is attributed to an increase in overall chain flexibility with the introduction of the *meta* linkages. It is well known that the incorporation of pendant groups also leads to an increase in T_g , however, in this case low crystallinity or amorphous polymers are obtained. To expand the application of PEKK, its melt processability and thermal properties need to be improved by reducing the melting temperature and increasing the glass transition temperature. To the best of our knowledge, the synthesis of PAEKs containing imide linkages in the main chains has not been reported in the open literature. Recently, we synthesized a new monomer containing imide linkages, bis [4-(*p*-phenoxybenzoyl)-1,2-benzenedioyl]-*N,N,N',N'*-4,4'-diaminodiphenyl ether (BPBDADPE), via simple synthetic procedures from readily available materials. In this paper, we synthesized novel PAEKs containing imide linkages in the main chains (PEK-I) by the electrophilic Friedel–Crafts solution copolycondensation of terephthaloyl chloride (TPC) with a mixture of diphenyl ether (DPE) and BPBDADPE in the presence of anhydrous aluminum chloride and *N*-methylpyrrolidone (NMP) in 1,2-dichloroethane (DCE). These polymers are expected to have the advantages of both PAEKs and polyimides in properties and semicrystalline copolymers with high T_g s and moderate T_m s could be obtained by the incorporation of lower content of BPBDADPE into the all-*para* backbone of *p*-PEKK. The polymers were characterized by FTIR, wide-angle X-ray diffraction (WAXD), differential scanning calorimeter (DSC), and thermal gravimetric analysis (TGA).

Experimental

Materials

All reagents and solvents were of analytical grade and were used without further purification unless stated otherwise. Terephthaloyl chloride (TPC, Shuanglin Chemical Co., Nanchang, China) was 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), 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 prior to use. 4,4'-Diaminodiphenyl ether (Shanghai Chemical Reagent) and trimellitic anhydride (Shanghai Chemical Reagent) were used as received. Bis(4-chloroformyl-1,2-benzenedioyl)-*N,N,N',N'*-4,4'-diaminodiphenyl ether (BCBDADPE) was prepared according to a literature procedure [25].

Monomer synthesis

To a 150 mL, three-necked, round-bottomed flask equipped with a mechanical stirrer, a thermometer, nitrogen inlet and outlet tubes, were added anhydrous AlCl_3 (13.08 g,

98 mmol) and DCE (30 mL). The flask was cooled to 0 °C using an ice-water bath, then a solution of NMP (2.066 g, 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 BCBDADPE (5.85 g, 10 mmol) and DPE (6.80 g, 40 mmol) with stirring and the reaction mixture was warmed to 20 °C over 2 h and the reaction was continued at this temperature for 4 h. The reaction mixture was quenched with methanol (50 mL) at 0 °C and the precipitate was crushed, washed with methanol, and extracted with boiling methanol for 24 h. The crude product was recrystallized from DMF/EtOH ($V_{\text{DMF}}/V_{\text{EtOH}} = 6:1$) and dried under vacuum at 100 °C to afford 6.94 g of white crystals (BPBDADPE). Yield: 81%. Mp: 212–213 °C. IR (KBr, cm^{-1}): 3065, 1779, 1721, 1660, 1586, 1500, 1377, 1245, 1165, 725; ^1H NMR (CDCl_3 , δ , ppm): 8.28 (s, 2H), 8.20 (d, $J = 7.6$ Hz, 2H), 8.09 (d, $J = 7.6$ Hz, 2H), 7.83 (d, $J = 8.8$ Hz, 4H), 7.47–7.41 (m, 8H), 7.25–7.20 (m, 6H), 7.13 (d, $J = 8.0$ Hz, 4H), 7.07 (d, $J = 8.8$ Hz, 4H); ^{13}C NMR (CDCl_3 , δ , ppm): 193.27, 166.53, 166.51, 162.69, 156.58, 155.12, 143.99, 135.62, 134.00, 132.59, 131.72, 130.45, 130.20, 128.15, 126.81, 125.00, 124.62, 123.95, 120.45, 119.64, 117.35; Anal. Calcd. for $\text{C}_{54}\text{H}_{32}\text{N}_2\text{O}_9$: C, 76.05; H, 3.78; N, 3.28. Found: C, 75.76; H, 3.56; N, 3.15.

Polymer synthesis

To a 100 mL, three-necked, round-bottomed flask equipped with a mechanical stirrer, a thermometer, nitrogen inlet and outlet tubes, were added anhydrous AlCl_3 (5.34 g, 40 mmol) and DCE (15 mL). The flask was cooled to 0 °C using an ice-water bath, then a solution of NMP (1.58 g, 16 mmol) in DCE (5 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 BPBDADPE (0.853 g, 1 mmol), DPE (0.680 g, 4 mmol), and TPC (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 DPE (0.1 mL) 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 III. Other polymers were also obtained by varying the molar ratio of DPE to BPBDADPE in a similar manner.

Characterization

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 ^{13}C NMR (100 MHz) spectra were obtained with a Bruker PC-A400 (400 MHz) spectrometer at an operating temperature of 25 °C using CDCl_3 as a solvent. Inherent viscosities were obtained with a concentration of 0.2 g/dL in 95% H_2SO_4 at 25 °C using an Ubbelohde suspended level viscometer. Differential scanning

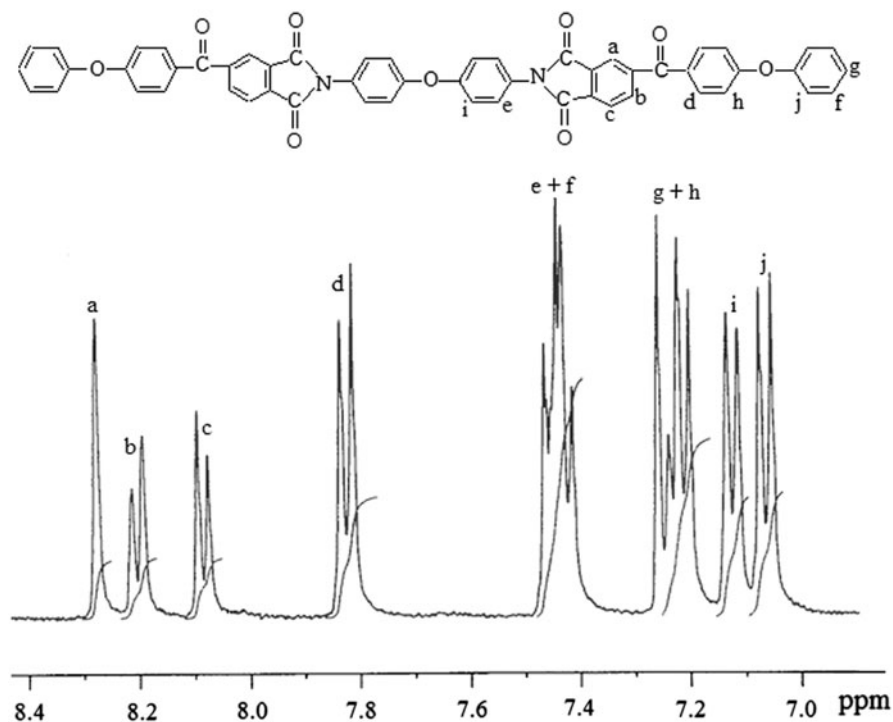


Fig. 1 ^1H NMR spectrum of BPBDADPE

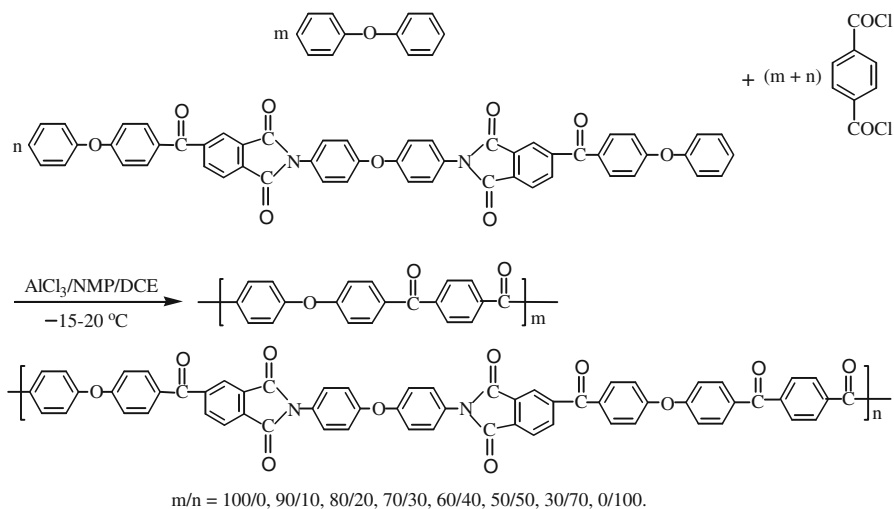
structure. The ^{13}C NMR spectrum of BPBDADPE shows 21 peaks corresponding to the 21 distinguishable carbons.

Synthesis and characterization of polymers

A series of novel PAEKs containing imide linkages in the main chains (PEK-I) were synthesized by electrophilic Friedel–Crafts solution copolycondensation of TPC with a mixture of DPE and BPBDADPE, over a wide range of DPE/BPBDADPE 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. 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 PAEKs [26]. 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_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 solubilization property of the Lewis acid (AlCl_3)/Lewis base complex is particularly significant in the preparation of *para*-linked PAEKs. The preparation of PAEKs 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 to -5 °C has been found to be particularly effective. Thereafter, the reaction temperature is slowly increased and maintained at room temperature.

In the synthesis of novel PAEKs containing imide linkages in the main chains (PEK-I), different molar ratios of DPE to BPBDADPE were taken to obtain the copolymers. But the sum of moles of DPE and BPBDADPE should be equal to that of TPC, which would produce a high molecular weight according to the modified Carothers equation, i.e., $X_n = (1 + r)/(1 - r)$, where X_n is the number-average degree of polymerization and r is the sum of the molar ratio of both DPE and BPBDADPE to TPC. The molar ratios and inherent viscosities of the polymers are given in Table 1. The inherent viscosity (η_{inh}) values of the polymers are above 0.62 dL/g and decreased with increase in concentration of BPBDADPE in polymer.



Scheme 2 Synthesis of the polymers

Table 1 Polymerization results

Polymer	DPE (mol%)	BPBDADPE (mol%)	Yield (%)	η_{inh}^a (dL/g)
I	100	0	95	0.78
II	90	10	94	0.75
III	80	20	94	0.73
IV	70	30	95	0.72
V	60	40	96	0.69
VI	50	50	95	0.68
VII	30	70	94	0.66
VIII	0	100	96	0.62

Polymerized at 20 °C with 5 mmol of TPC and 5 mmol of (DPE + BPBDADPE) in 20 mL of DCE for 20 h

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

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 were higher 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 polymers show no absorption at about 1740 cm^{-1} indicating the absence of $-\text{COCl}$ groups. All the spectra of the polymers except for the polymer I without BPBDADPE show characteristic bands around 1780 cm^{-1} due to imide $\text{C}=\text{O}$ asymmetrical stretch, around 1722 cm^{-1} due to imide $\text{C}=\text{O}$ symmetrical stretch, around 1659 cm^{-1} due to aromatic ketone $\text{C}=\text{O}$ stretch, around 1377 cm^{-1} due to imide $\text{C}-\text{N}$ stretch, and around 1245 cm^{-1} due to $\text{Ar}-\text{O}-\text{Ar}$ stretch. The FT-IR spectrum of the polymer VI is shown in Fig. 2.

Properties of polymers

The crystallinities of the polymers were evaluated by WAXD. The WAXD patterns of the polymers I–VIII are presented in Fig. 3. 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) [14]. As shown in Fig. 3, the WAXD patterns of the polymers II–V with 60–90 mol% DPE fundamentally bore the same number and site of diffraction peak of every crystal facecrystal plane in comparison with that of the *p*-PEKK, but the diffraction peaks decreased in intensity with the increase in BPBDADPE content due to the incorporation of imide linkages in the main chains, which disrupted the regularity of molecular chains and inhibited the close packing of the polymer chains. When the molar ratio of BPBDADPE to DPE was up to 50/50, the polymer VI obtained was amorphous and no obvious diffraction peak was observed. The polymers VII and VIII with 70–100 mol% BPBDADPE were also amorphous and showed only one diffuse diffraction peak. The aforementioned results indicated that the polymers II–V had the chain similar to that of the polymer I (*p*-PEKK) to form the crystal that was included in the orthorhombic system with the *p*-PEKK.

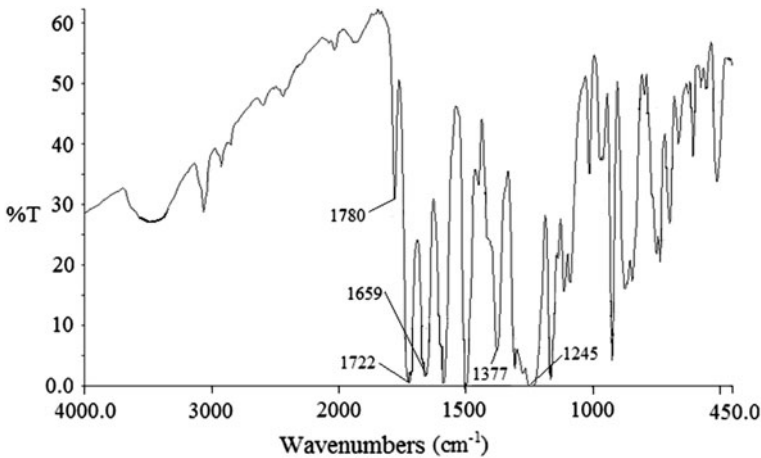
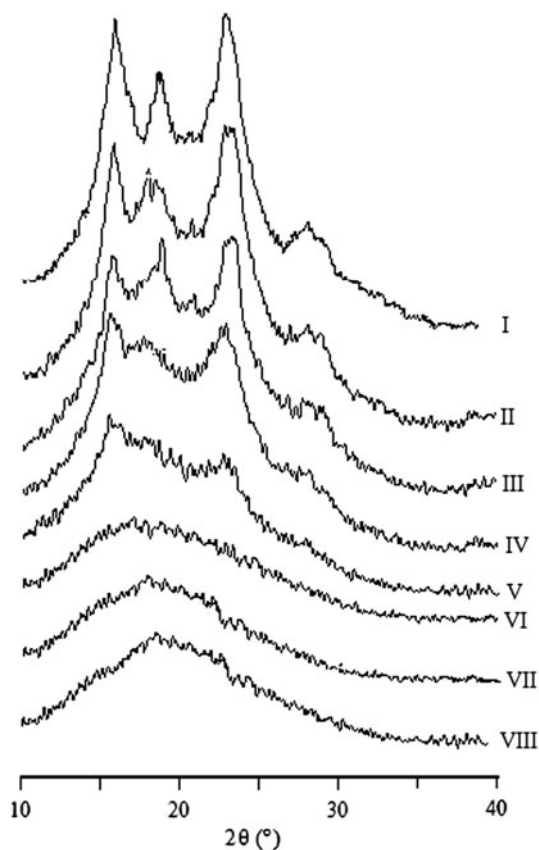


Fig. 2 FT-IR spectrum of polymer VI

The thermal properties of the polymers were evaluated by DSC and TGA and the results are given in Table 2. 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 II–VII were 177–187 °C, which exhibited much higher T_g s than those of commercially available PEEK and PEKK (70/30), T_g s of which were 143 and 156 °C, respectively. This attributed to the presence of rigid and highly polar imide linkages in the polymers. The polymer I (*p*-PEKK) with 100 mol% DPE had the lowest T_g of 170 °C and the polymer VIII with 100 mol% BPBDADPE had the highest T_g of 190 °C. The increased T_g values of the polymers II–VIII can be explained by the fact that the intermolecular interaction force was enhanced and the segmental motion was hindered due to the presence of rigid and highly polar imide linkages in the main chains. The crystalline temperatures (T_c s) of the polymers I–V were 195–257 °C and also increased with the increase in concentration of BPBDADPE in the polymer. The T_m s of the polymers I–V with 60–100 mol% DPE were 341–384 °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–V decreased gradually with the increase in concentration of BPBDADPE in the polymer due to the decrease in regularity of molecular chains with the introduction of imide linkages in the main chains. When the molar ratio of BPBDADPE to DPE was up to 50/50, no melting endothermic peak was observed from DSC curve of the resulting polymer VI. The polymers VII and VIII with 70–100 mol% BPBDADPE 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 polymers IV and V with 30–40 mol% BPBDADPE had not only high T_g s of 182–183 °C, but also moderate T_m s of 341–343 °C, having good potential for the melt processing. DSC curves of the polymers I–VIII are illustrated in Fig. 4.

Fig. 3 WAXD patterns of polymers I–VIII



The novel PAEKs containing imide linkages in the main chains (PEK-I) exhibited high thermal stability. As shown in Table 2, the temperatures at 5% weight loss (T_d s) of all the polymers were above 525 °C in N_2 . The T_d values of the polymers decreased with increase in BPBDADPE content in polymer since PAEKs had higher T_d s than aromatic poly(ether imide)s. The polymer I without

Table 2 Thermal properties of the polymers

Polymer	T_g (°C)	T_m (°C)	T_c (°C)	T_d (°C)
I	170	384	195	559
II	177	350	251	546
III	180	346	253	543
IV	182	343	254	533
V	183	341	257	532
VI	185			528
VII	187			526
VIII	190			525

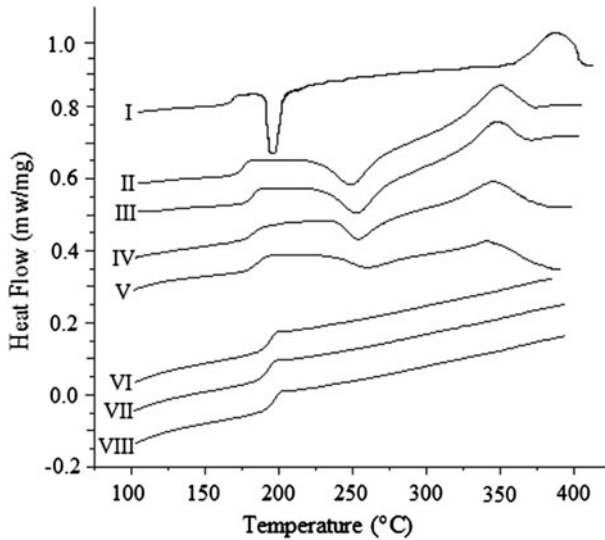


Fig. 4 DSC curves of polymers I–VIII

BPBDADPE had the highest T_d of 559 °C, while the polymer VIII with 100 mol% BPBDADPE had the lowest T_d of 525 °C. The semicrystalline polymers II–V had high T_d s of 532–546 °C. The temperature difference between T_m and T_d of the polymers IV and V was large, thus the melt processing can be easily accomplished. TGA curves of the polymers II, IV, and VIII are illustrated in Fig. 5.

The solubility behavior of the polymers prepared in this study was examined by measuring dimensional changes of the polymer thin films immersed in aggressive solvent at room temperature for 24 h and the results are listed in Table 3. As shown in Table 3, the polymer I (*p*-PEKK) and polymer II had excellent resistance to organic solvents. The polymers III–VII were insoluble in highly polar solvents such as NMP, DMAc, DMSO, and DMF except for concentrated sulfuric acid, but they can be swelled in NMP, DMAc, and DMF. The polymers IV–VII can be swelled in all of the highly polar solvents. The polymer VIII with 100 mol% BPBDADPE was soluble in NMP. However, the polymers III–VII were 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 resistance to solvents of the polymers II–VIII decreased gradually with the increase in concentration of BPBDADPE in the polymer, the semicrystalline polymers III–V had good resistance to common organic solvents, but the resistance to highly polar solvents of them was poor compared with PEEK or PEKK.

The mechanical properties of the polymers I–VIII were measured and the results are presented in Table 4. From these data, it can be seen that the semicrystalline copolymers II–V had tensile strengths of 99.7–103.6 MPa, Young's moduli of 2.18–2.47 GPa, and elongations at break of 14.2–17.7%, indicating that they are strong materials. The tensile strengths and Young's moduli of amorphous polymers VI–VIII were lower than those of semicrystalline polymers I–V.

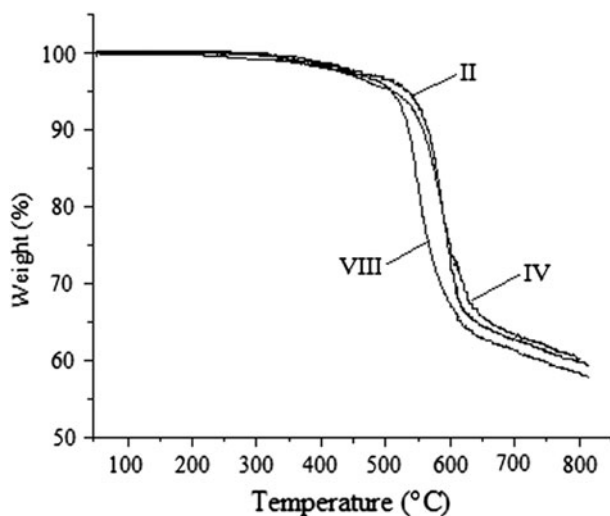


Fig. 5 TGA curves of polymers II, IV, and VIII

Table 3 Solubility of polymers

Polymer	H ₂ SO ₄	NMP	DMAc	DMSO	DMF	THF	CHCl ₃	DCE	EtOH
I	+	–	–	–	–	–	–	–	–
II	+	–	–	–	–	–	–	–	–
III	+	+–	+–	–	+–	–	–	–	–
IV	+	+–	+–	+–	+–	–	–	–	–
V	+	+–	+–	+–	+–	–	–	–	–
VI	+	+–	+–	+–	+–	–	–	–	–
VII	+	+–	+–	+–	+–	–	–	–	–
VIII	+	+	+–	+–	+–	–	–	–	–

The solubility was tested with the polymer thin films immersed in the solvent at room temperature for 24 h

+: soluble, +–: swollen, –: insoluble

Conclusion

In summary, a series of novel PAEKs containing imide linkages in the main chains (PEK-I) were conveniently synthesized by the modified electrophilic Friedel–Crafts solution copolycondensation of TPC with a mixture of DPE and BPBDADPE, over a wide range of DPE/BPBDADPE molar ratios, under very mild conditions. The T_g s of the semicrystalline polymers II–V were 177–183 °C, which exhibited much higher T_g s than those of commercially available PEEK and PEKK (70/30), T_g s of which were 143 and 156 °C, respectively. The T_m values of the polymers decreased and then disappeared with increasing BPBDADPE content. The T_m (384 °C) of the *p*-PEKK homopolymer can be reduced to 341 °C when the molar ratio of

Table 4 Mechanical properties of polymers II-V

Polymer	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)
I	102.9	2.24	14.8
II	103.6	2.18	17.7
III	101.8	2.47	14.2
IV	102.5	2.33	15.4
V	99.7	2.26	16.1
VI	87.4	2.11	18.8
VII	82.6	1.92	21.5
VIII	77.9	1.67	25.3

BPBDADPE to DPE is 40/60, moreover the glass transition temperature of the resulting polymer V can be up to 183 °C, 13 °C higher than that of *p*-PEKK. The polymers IV and V with 30–40 mol% BPBDADPE had not only high T_g s of 182–183 °C, but also moderate T_m s of 341–343 °C, having good potential for the melt processing. But it should be pointed out that the polymers IV and V would no longer be a significant competitor for PEEK or PEKK because of inferior solvent resistance. The polymers IV and V had tensile strengths of 99.7–102.5 MPa, Young's moduli of 2.26–2.33 GPa, and elongations at break of 15.4–16.1% and exhibited high thermal stability and good resistance to common organic solvents.

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