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ORIGINAL PAPER

Synthesis and characterization of novel copolymers of poly(ether ketone ketone) and poly(ether ketone sulfone imide)

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Abstract A new monomer containing sulfone and imide linkages, bis{4-[4-(*p*-phenoxyphenylsulfonylphenoxy)benzoyl]-1,2-benzenedioyl}-*N*,*N*,*N*′,*N*′-4,4′-diaminodiphenyl ether (BPSPBDADPE), was prepared by the Friedel–Crafts reaction of bis(4-chloroformyl-1,2-benzenedioyl)-*N*,*N*,*N*′,*N*′-4,4′-diaminodiphenyl ether with 4,4′-diphenoxydiphenyl sulfone. Novel copolymers of poly(ether ketone ketone) and poly(ether ketone sulfone imide) were synthesized by electrophilic Friedel–Crafts solution copolycondensation of terephthaloyl chloride with a mixture of DPE and BPSPBDADPE. The polymers were characterized by different physico-chemical techniques. The polymers with 10–25 mol% BPSPBDADPE are semicrystalline and had increased T_gs over commercially available PEEK and PEKK (70/30) due to the incorporation of sulfone and imide linkages in the main chains. The polymer IV with 25 mol% BPSPBDADPE had not only high T_g of 194 °C but also moderate T_m of 338 °C, having good potential for melt processing and exhibited high thermal stability and good resistance to common organic solvents.

Keywords Poly(ether ketone ketone) · Electrophilic copolycondensation · Poly(ether ketone sulfone imide) · Terephthaloyl chloride · Thermal property

Introduction

Poly(aryl ether ketone)s (PAEKs) are a family of semicrystalline, 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

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aerospace, automobile, electronics, and other high technology fields [1–3]. There are two general synthetic pathways to producing PAEKs [4–6]. The first approach involves the nucleophilic aromatic displacement of carbonyl-activated halides by phenoxide anions [7–11]. The second one involves 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 a variety 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. The high cost, high processing temperatures, and relatively low glass transition temperatures are the main drawbacks of PAEKs. The use of PAEK materials with higher glass transition temperatures is desirable in advanced composite applications.

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. Taking into account 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. 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 [18–20]. However, the improvement of T_g is not so marked for those reported PEEK copolymers. Shibata et al. [21] reported the synthesis of the block copolymers of the PEEK and the poly(aryl ether sulfone) containing biphenylene moiety (PEBS). 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 380 °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 [22], 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 enhancing the glass transition temperature. To the best of our knowledge, the synthesis of copolymers of PEKK and poly(ether ketone sulfone imide) (PEKSI) has not been reported in the open literature. Recently, we synthesized a new monomer containing sulfone and imide linkages, bis{4-[4-(*p*-phenoxyphenylsulfonylphenoxy)benzoyl]-1,2-benzenedioyl}-*N*,*N*,*N*′,*N*′-4,4′-diaminodiphenyl ether (BPSPBDADPE), via simple synthetic procedures from readily available materials. In this article, we synthesized novel copolymers of PEKK and PEKSI by electrophilic Friedel–Crafts solution copolycondensation of terephthaloyl chloride (TPC) with a mixture of diphenyl ether (DPE) and BPSPBDADPE 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 poly(ether sulfone imide)s in properties and semicrystalline copolymers with high T_gs and moderate T_ms could be obtained by the incorporation of lower content of BPSPBDADPE into the all-*para* backbone of *p*-PEKK. The polymers were characterized by FT-IR, wide-angle X-ray diffraction (WAXD), differential scanning calorimeter (DSC), and thermogravimetric analysis (TGA).

Experimental

Materials

All reagents and solvents were of analytical grade and were used without further purification unless stated otherwise. TPC (Shuanglin Chemical Co., Nanchang, China) was purified by distillation under vacuum prior to use. DCE (Shanghai Chemical Reagent), NMP (Shanghai Chemical Reagent), *N,N*-dimethylacetamide (DMAc, Shanghai Chemical Reagent), 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 [23].

Monomer synthesis

To a 150 mL, three-necked, round-bottomed flask equipped with a mechanical stirrer, a thermometer, nitrogen inlet and outlet tubes, anhydrous $AlCl_3$ (22.03 g, 165 mmol) and DCE (50 mL) were added. 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, BCBDADPE (5.85 g, 10 mmol) and 4,4′-diphenoxydiphenyl sulfone (DPODPS) (16.08 g, 40 mmol) were added 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 ($V_{DMF}/V_{EtOH} = 4{:}1$) and dried under vacuum at 100 °C to afford 10.13 g of white crystals (BPSPBDADPE). Yield: 77 %. Mp: 166–167 °C. IR (KBr, cm^{-1}): 3067, 1779, 1721, 1658, 1583, 1501, 1376, 1327, 1244, 1165, 727; ^{1}H NMR ($CDCl_3$, δ, ppm): 8.28 (s, 2H), 8.22 (d, $J = 8.0$ Hz, 2H), 8.10 (d, $J = 8.0$ Hz, 2H), 7.96 (d, $J = 8.8$ Hz, 4H), 7.91–7.83 (m, 8H), 7.46 (d, $J = 9.2$ Hz, 4H), 7.40 (t, $J = 7.8$ Hz, 4H), 7.24–7.13 (m, 14H), 7.07–7.02 (m, 8H); ^{13}C NMR ($CDCl_3$, δ, ppm): 193.09, 166.44, 166.38, 162.21, 160.24, 159.82, 156.59, 154.90, 143.48, 137.57, 135.65, 135.03, 132.66, 131.81, 130.21, 130.17, 130.02, 129.90, 129.73, 128.13, 126.80, 125.14, 124.61, 124.04, 120.38, 119.63, 119.53, 119.09, 117.77; Anal. Calcd. for $C_{78}H_{48}N_2O_{15}S_2$: C, 71.12; H, 3.67; N, 2.13. Found: C, 70.88; H, 3.46; N, 2.19.

Polymer synthesis

To a 100 mL, three-necked, round-bottomed flask equipped with a mechanical stirrer, a thermometer, nitrogen inlet and outlet tubes, anhydrous $AlCl_3$ (5.87 g, 44 mmol) and DCE (15 mL) were added. 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 BPSPBDADPE (1.317 g, 1 mmol), DPE (0.680 g, 4 mmol), and TPC (1.015 g, 5 mmol) were added 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 BPSPBDADPE 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. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were obtained with a Bruker Avance (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 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.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 having dimensions of 4.0 × 6.0 × 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. WAXD was measured with a Rigaku D/MAX-IIA X-ray diffractometer, using CuKα 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

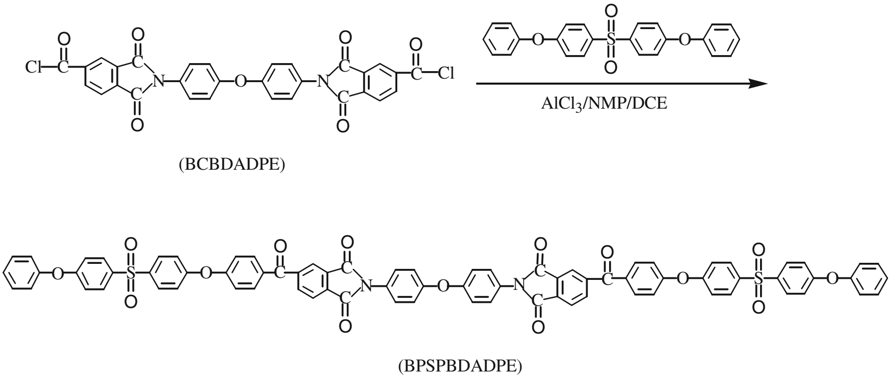
Synthesis of monomer containing sulfone and imide linkages

The route to the synthesis of a new monomer containing sulfone and imide linkages, BPSPBDADPE, is shown in Scheme 1. BPSPBDADPE was conveniently prepared by the Friedel–Crafts reaction of BCBDADPE with DPODPS and could be obtained as a pure material after recrystallization from DMF/EtOH.

FT-IR, NMR spectroscopies, and elemental analysis were used to confirm the structure of BPSPBDADPE. In the FT-IR spectrum, the key structural features include the following absorptions: imide C=O asymmetrical stretch, 1779 cm^{-1}, imide C=O symmetrical stretch, 1721 cm^{-1}, aromatic ketone C=O stretch, 1658 cm^{-1}, imide C–N stretch, 1376 cm^{-1}, sulfone S=O stretch, 1327 and 1165 cm^{-1}, Ar–O–Ar stretch, 1244 cm^{-1} and imide C=O bend, 727 cm^{-1}. In the ^{1}H NMR spectrum, the assignments of the peaks are in good agreement with the proposed monomer structure. The ^{13}C NMR spectrum of BPSPBDADPE shows 29 peaks corresponding to the 29 distinguishable carbons.

Synthesis and characterization of polymers

A series of novel PEKK/PEKSI copolymers were synthesized by electrophilic Friedel–Crafts solution copolycondensation of TPC with a mixture of DPE and BPSPBDADPE, over a wide range of DPE/BPSPBDADPE molar ratios, as shown in Scheme 2. It is generally accepted that premature polymer precipitation from

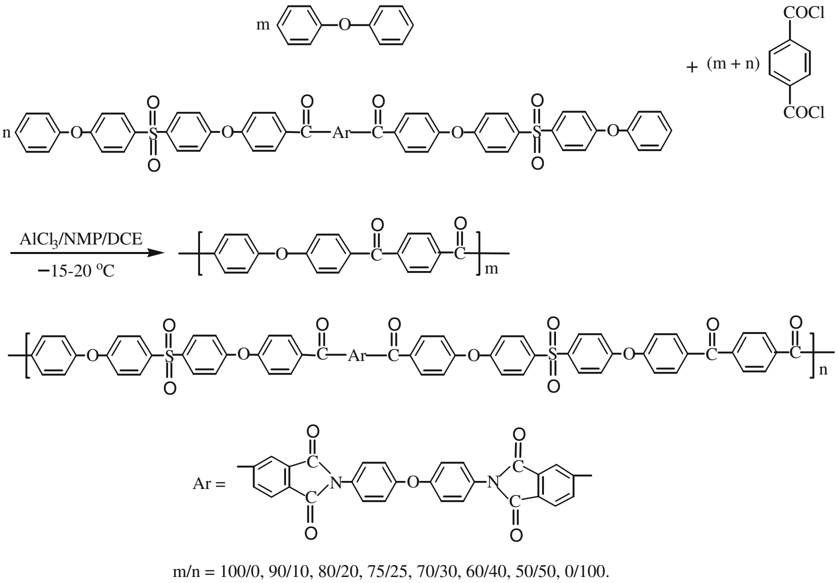


Scheme 1 Synthetic route of BPSPBDADPE

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. [24] 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. 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 crosslinking. Suppression of side reactions results in a thermally stable polymer that does not degrade or crosslink 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 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 PEKK/PEKSI copolymers, different molar ratios of DPE to BPSPBDADPE were taken to obtain the copolymers. But the sum of moles of DPE and BPSPBDADPE 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 BPSPBDADPE 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 0.72 dL/g and increased with increase in concentration of BPSPBDADPE in polymer. 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 1,740 cm^{-1} indicating the absence of –COCl groups. All the spectra of the polymers except for the polymer I without BPSPBDADPS show characteristic bands around 1,780 cm^{-1} due to imide C=O asymmetrical stretch, around 1,722 cm^{-1} due to



Scheme 2 Synthesis of the polymers

Table 1 Polymerization results

Polymer	DPE (mol%)	BPSPBDADPE (mol%)	Yield (%)	η_{inh}^{a} (dL/g)
I	100	0	94	0.72
II	90	10	95	0.77
III	80	20	95	0.80
IV	75	25	94	0.82
V	70	30	96	0.85
VI	60	40	95	0.89
VII	50	50	96	0.91
VIII	0	100	96	0.94

Polymerized at 20 °C with 5 mmol of TPC and 5 mmol of (DPE + BPSPBDADPE) 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

imide C=O symmetrical stretch, around 1,658 cm^{-1} due to aromatic ketone C=O stretch, around 1,376 cm^{-1} due to imide C–N stretch, around 1,306 and 1,151 cm^{-1} due to sulfone S=O stretch, and around 1,245 cm^{-1} due to Ar–O–Ar stretch. The FT-IR spectrum of the copolymer VI is shown in Fig. 1.

Properties of polymers

The crystallinities of the polymers were evaluated by WAXD. The WAXD patterns of the polymers I–V and VIII are presented in Fig. 2. It is well documented that the

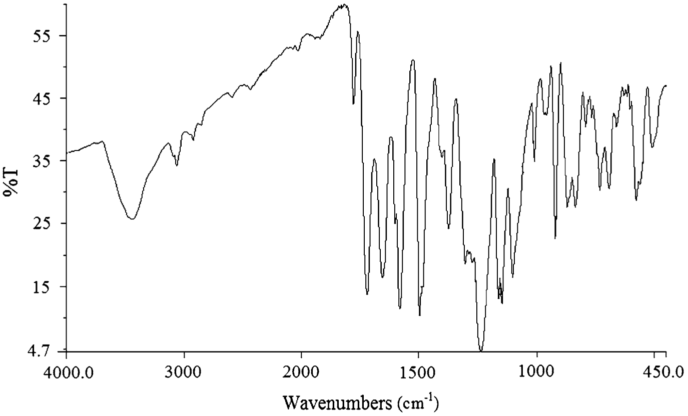
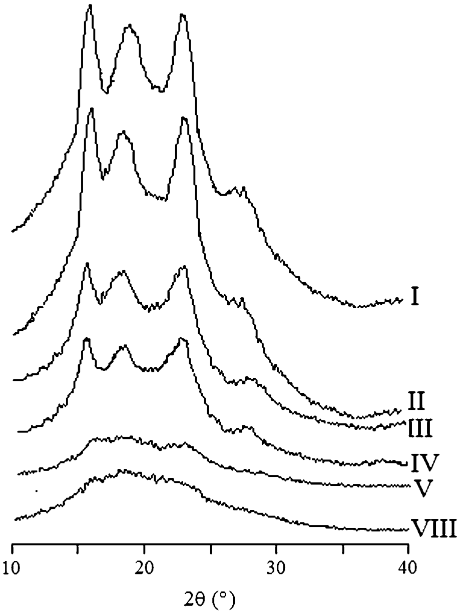


Fig. 1 FT-IR spectrum of polymer VI

Fig. 2 WAXD patterns of polymers I–V and VIII



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. 2, the WAXD patterns of the polymers II–IV with 75–90 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 BPSPBDADPE content due to the incorporation of sulfone and 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 BPSPBDADPE to DPE was up to 30/70, the polymer V obtained was amorphous and no obvious diffraction peak was observed. The polymers VI–VIII with 40–100 mol% BPSPBDADPE were also amorphous and showed only one diffuse diffraction peak. The aforementioned results indicated that the polymers II–IV 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.

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 N_2, quenched to −50 °C and rerun to obtain T_g. The T_gs of the polymers II–VII were 183–204 °C, which exhibited much higher T_gs than those of commercially available PEEK and PEKK (70/30), T_gs of which were 143 and 156 °C, respectively. This attributed to the presence of highly polar sulfone and imide linkages in the polymers. The polymer I (*p*-PEKK) with 100 mol% DPE had the lowest T_g of 169 °C and the polymer VIII with 100 mol% BPSPBDADPE had the highest T_g of 218 °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 highly polar sulfone and imide linkages in the main chains. The crystalline temperatures (T_cs) of the polymers I–IV were 195–265 °C and also increased with the increase in concentration of BPSPBDADPE in the polymer. The T_m's of the polymers I–IV with 75–100 mol% DPE were 338–380 °C and the polymer I (*p*-PEKK) with 100 mol% DPE had the highest T_m of 380 °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 BPSPBDADPE in the polymer due to the decrease in regularity of molecular chains with the incorporation of sulfone and imide linkages in the main chains. When the molar ratio of BPSPBDADPE to DPE was up to 30/70, no melting endothermic peak was observed from DSC curve of the resulting polymer V. The polymers VI–VIII with 40–100 mol% BPSPBDADPE 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 169 °C, but its too high T_m of 380 °C made it unsuitable for the melt processing. However, the copolymer IV with 25 mol% BPSPBDADPE had not only high T_g of 194 °C but also moderate T_m of 338 °C, having good potential for the melt processing. DSC curves of the polymers I–VIII are illustrated in Fig. 3.

Table 2 Thermal properties of the polymers

Polymer	T_g (°C)	T_m (°C)	T_c (°C)	T_d (°C)
I	169	380	195	559
II	183	352	251	543
III	190	345	260	535
IV	194	338	265	529
V	197			526
VI	200			520
VII	204			516
VIII	218			508

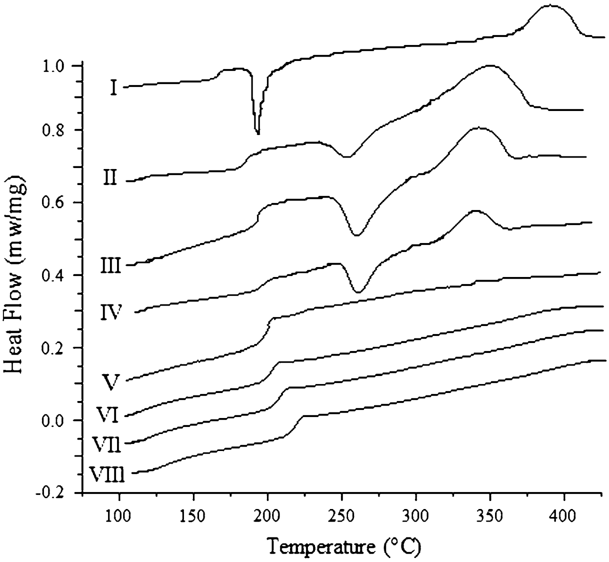


Fig. 3 DSC curves of polymers I-VIII

The novel PEKK/PEKSI copolymers exhibited high thermal stability. As shown in Table 2, the temperatures at 5 % weight loss (T_ds) of all the polymers were above 508 °C in N_2. The T_d values of the polymers decreased with increase in BPSPBDADPE content in polymer since PAEKs had higher T_ds than aromatic poly(ether ketone sulfone imide)s. The polymer I without BPSPBDADPE had the highest T_d of 559 °C, while the polymer VIII with 100 mol% BPSPBDADPE had the lowest T_d of 508 °C. The semicrystalline polymers II–IV had high T_ds of 529–543 °C. The temperature difference between T_m and T_d of the copolymer IV was large, thus the melt processing can be easily accomplished. Typical TGA curve of copolymer IV is illustrated in Fig. 4.

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 V–VII can be swelled in all of the highly polar solvents. The polymer VIII with 100 mol% BPSPBDADPE 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 BPSPBDADPE in the polymer, the semicrystalline polymers III and IV had good resistance to common organic solvents, but the resistance to highly polar solvents of them was poor compared with PEEK or PEKK.

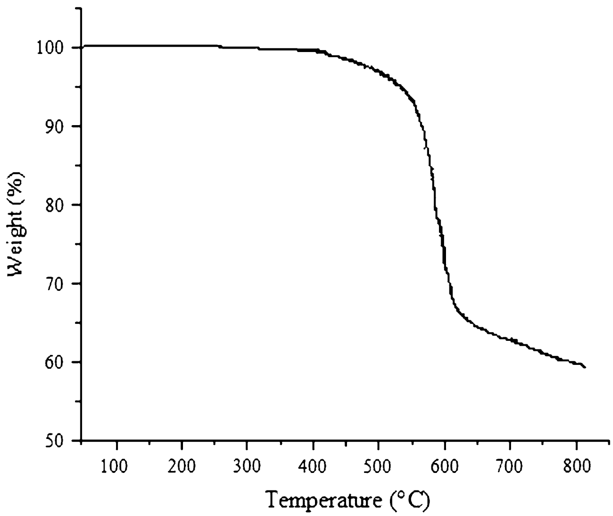


Fig. 4 TGA curve of polymer IV

Table 3 Solubility of polymers

Polymer	H_2SO_4	NMP	DMAc	DMSO	DMF	THF	$CHCl_3$	DCE	EtOH
I	+	−	−	−	−	−	−	−	−
II	+	−	−	−	−	−	−	−	−
III	+	+−	−	−	−	−	−	−	−
IV	+	+−	+−	−	+−	−	−	−	−
V	+	+−	+−	+−	+−	−	−	−	−
VI	+	+−	+−	+−	+−	−	−	−	−
VII	+	+−	+−	+−	+−	−	−	−	−
VIII	+	+	+−	+−	+−	−	+−	+−	−

+ soluble, +− swollen, − insoluble

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

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–IV had tensile strengths of 101.1–102.5 MPa, Young's moduli of 2.19–2.38 GPa, and elongations at break of 13.9–16.1 %, indicating that they are strong materials. The tensile strengths and Young's moduli of amorphous polymers V–VIII were lower than those of semicrystalline polymers I–IV.

Conclusion

In summary, a series of novel PEKK/PEKSI copolymers were conveniently synthesized by the modified electrophilic Friedel–Crafts solution copolycondensation

Table 4 Mechanical properties of polymers I-VIII

Polymer	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)
I	102.9	2.24	14.8
II	102.5	2.21	15.4
III	101.6	2.38	13.9
IV	101.1	2.19	16.1
V	89.6	2.14	16.5
VI	85.4	2.03	19.6
VII	80.7	1.87	22.8
VIII	76.8	1.64	27.7

of TPC with a mixture of DPE and BPSPBDADPE, over a wide range of DPE/BPSPBDADPE molar ratios, under very mild conditions. The T_gs of the semicrystalline polymers II–IV were 183–194 °C, which exhibited much higher T_gs than those of commercially available PEEK and PEKK (70/30), T_gs of which were 143 and 156 °C, respectively. The T_m values of the polymers decreased and then disappeared with increasing BPSPBDADPE content. The T_m (380 °C) of the *p*-PEKK homopolymer can be reduced to 338 °C when the molar ratio of BPSPBDADPE to DPE is 25/75; moreover, the glass transition temperature of the resulting polymer IV can be up to 194 °C, 25 °C higher than that of *p*-PEKK. The polymer IV with 25 mol% BPSPBDADPE had not only high T_g of 194 °C but also moderate T_m of 338 °C, having good potential for the melt processing. The polymer IV had tensile strength of 101.1 MPa, Young's modulus of 2.19 GPa, and elongation at break of 16.1 % and exhibited high thermal stability and good resistance to common organic solvents.

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