

Synthesis and Properties of Organic Soluble Semicrystalline Poly(aryl ether ketone)s Copolymers Containing Phthalazinone Moieties

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ABSTRACT: A series of poly(aryl ether ketone)s (PAEK) copolymers containing phthalazinone moieties were synthesized by modest polycondensation reaction from 4-(4-hydroxyl-phenyl)-(2*H*)-phthalazin-1-one (DHPZ), hydroquinone (HQ), and 1,4-bis(4-fluorobenzoyl)benzene (BFBB). The T_g values of these copolymers ranged from 168 to 235°C, and the crystalline melting temperatures varied from 285 to 352°C. By introducing phthalazinone moieties into the main chain, the solubility of these copolymers was improved in some common polar organic solvents, such as chloroform (CHCl₃), *N*-methyl-2-pyrrolidinone (NMP), nitrobenzene (NB) and so on. The values of 5% weight loss temperatures were all higher than 510°C in nitrogen. The crystal structures of these copolymers were deter-

mined by wide-angle X-ray diffraction (WAXD), which revealed that they were semicrystalline in nature, and the crystal structure of these copolymers was orthorhombic, equal to poly(ether ether ketone)s. As phthalazinone content in the backbone varied from 0 to 40 mol % (mole percent), the cell parameters of these copolymers including the *a*, *b*, and *c* axes lengths ranged from 7.76 to 7.99 Å, 6.00 to 6.14 Å, and 10.10 to 10.19 Å, respectively. The degree of crystallinity (via differential scanning calorimetry) decreased from 37.70% to 16.14% simultaneously. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 1744–1753, 2007

Key words: phthalazinone; crystal structures; crystallization; poly(ether ketone)s; copolymerization

INTRODUCTION

Poly(aryl ether ketone)s (PAEK) have been known as a kind of high-performance engineering thermoplastics because of their unique high chemical resistance and excellent mechanical properties that are retained at high temperatures.^{1–3} As a member of PAEK family, poly(ether ether ketone)s (PEEK) has a chemical structure with a regular sequence of ether and ketone units, two at a time.

PEEK's glass transition temperature (T_g) and the crystalline melting temperature (T_m) are 162 and 362°C, respectively.⁴ Therefore its application temperature can be up to 260°C, which is higher than that of poly(ether ether ketone)s (PEEK) commercialized by ICI. It should have the wider application fields than PEEK. Unfortunately, the utility of PEEK is limited due to its high processing temperature (above 430°C), and its very poor solubility (PEEK can only be

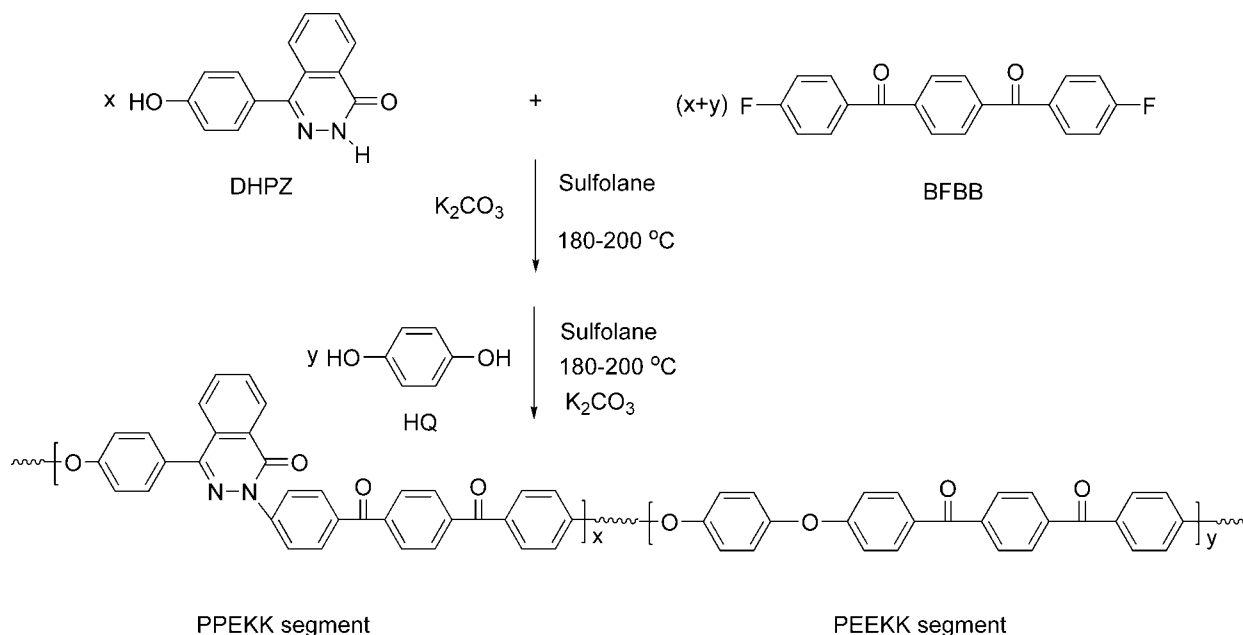
soluble in concentrated sulfuric acid at room temperature^{4–6}). Up to now, investigations on the modifications of PEEK generally aim at decreasing its T_m values, studying its crystallization behaviors and researching its crystal structures.^{4–6} Meanwhile, there are few literatures on improving its solubility in some common organic solvents by copolymerization while maintaining its crystallinity and excellent thermal stability.

Phthalazinone structure has been found to be high efficiency unit for improving the solubility of high performance thermoplastics by Jian et al., and several kinds of PAEKs bearing crank and twisted noncoplanar phthalazinone moieties in the main chain have been reported.^{7–9} The solubilities of these polymers, which possessed excellent mechanical and thermal properties were improved in some common polar organic solvents. Some of them have been extensively applied as composite materials, membranes and insulating coatings, etc.^{10–12} For instance, poly(phthalazinone ether ketone)s (PPEKK) exhibited good solubility in some common polar organic solvents while maintaining excellent thermal and mechanical properties.

It is of our interest to synthesize organic soluble semicrystalline PAEK copolymers by incorporating

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Scheme 1 Synthesis route of PAEK copolymers.

phthalazinone moieties into the main chain of PEEKK and explore the crystal structures and solubility, as well as thermal stabilities of these copolymers. Herein, we report a series of PAEK copolymers derived from 1,4-bis(4-fluorobenzoyl)benzene (BFBB) with hydroquinone (HQ) and 4-(4-hydroxyphenyl)(2H)-phthalazin-1-one (DHPZ) by nucleophilic polycondensation reaction. The influences of incorporating phthalazinone structure into the main chain of the copolymers on T_g , T_m , thermal stabilities, crystallinity, and solubility were studied by the means of Fourier transform infrared (FTIR), NMR, Gel permeation chromatography (GPC), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), wide-angle X-ray diffraction (WAXD), and solubility experiments, respectively.

EXPERIMENTAL

Materials

Fluorobenzene (Liaoning Zhonghe Fine Chemical Plant) was distilled and kept over anhydrous CaCl_2 overnight before use. Anhydrous AlCl_3 (Yanbian Chemical Reagent Plant) and HQ (Beijing North suburb Chemical Plant) were all used as purchased. Anhydrous potassium carbonate (Tianjin Chemical Reagent Plant) was dried in vacuum at 100°C for 24 h before use. DHPZ was synthesized according to the procedure reported previously.⁸ The product was obtained as white powders; mp: $310\text{--}310.8^\circ\text{C}$; yield: 90 wt % (weight percent). BFBB was prepared according to the reported method.¹³ The product was obtained as white pellets; mp: $220.2\text{--}221.2^\circ\text{C}$; yield: 90 wt %.

Sulfolane (Tianjin Chemical Reagent Plant) was dried and distilled over sodium hydroxide pellets under reduced pressure, then the middle fractions were collected and stored over molecular sieves (Type 4 Å).

Synthetic procedure of PAEK copolymers

The synthetic route of PAEK copolymers was shown as Scheme 1. The number in the sample name indicated the molar fractions of the monomers. For example, the copolymer containing 60 mol % phthalazinone moieties and 40 mol % HQ was labeled as PAEK64. All of the PAEK copolymers were prepared in a similar procedure. Therefore, the typical synthesis of PAEK64 was described as follows.

The polycondensation reaction was carried out in a 100-mL three-necked round bottom flask outfitted with a mechanical stirrer, a nitrogen inlet, a Dean-Stark trap outfitted with a condenser and a nitrogen outlet. The flask was charged with a mixture of DHPZ (6.0 mmol), BFBB (10.0 mmol), potassium carbonate (8.4 mmol), 7 mL sulfolane, and 15 mL toluene. The reaction system was heated to a reflux temperature to promote phenolate formation. Subsequently the polymerization was conducted for 3–5 h. Then HQ (4.0 mmol), potassium carbonate (7.0 mmol), 4 mL sulfolane, and 15 mL toluene was added, and the same procedure described earlier was done. The resultant reaction mixture was slowly poured into hot water while stirring vigorously, and the resulting polymer precipitated out as a fine fiber. The dried polymer was further purified by dissolving in chloroform and being filtered through a thin layer of Celite. Then the filtrate was slowly poured into

ethanol while stirring, and the resulting suspension was filtered. Finally, the purified product was dried at 120°C under vacuum for 24 h. The yield was 93 wt %. The purification method of PAEK copolymers with phthalazinone content less than 60 mol % was different from that of PAEK64. For this method, the resultants were subjected to Soxhlet extraction with acetone overnight to produce white or yellow powders, and then these powders were dried under vacuum at 120°C for 24 h. The yield was 90 wt % or so.

Measurement

The weight loss fractions were obtained by extracting the resulting copolymers with chloroform, and measuring the weight of the residual copolymers or the copolymers precipitated from chloroform. The densities of all the PAEK copolymers were measured by the suspension method in a *n*-heptane/carbon tetrachloride mixture using a PZ-B-5 liquid-density balance. GPC analyses were carried out on a HP 1090 HPLC equipped with 5 μ m Phenogel columns (linear, 4 \times 500 Å) arranged in series with chloroform as solvent and a UV detector at 254 nm. The \bar{M}_n s of PAEK copolymers, which were insoluble in chloroform, were determined by ^{19}F NMR with the spectra being obtained by the use of a Varian Unity Inova 400 spectrometer operating at 376.067 MHz at 25°C. The sample solution (\sim 5%) in H_2SO_4 was prepared at room temperature, with sodium trifluoroacetate used as the internal standard. IR absorption spectra were recorded by reflection method with a Thermo Nicolet Nexus 470 Fourier transform infrared (FTIR) spectrometer. ^1H NMR spectra were obtained with a Varian Unity Inova 400 spectrometer at an operating temperature of 25°C using CDCl_3 as

a solvent and were listed in parts per million downfield from tetramethylsilane (TMS). TGA and derivative thermogravimetric analysis (DTG) of PAEK copolymers were performed on a Mettler TGA/SDTA851 thermogravimetric analysis instrument in a nitrogen atmosphere at a heating rate of 20°C min^{-1} from 200 to 800°C. Decomposition temperature (T_d) was taken as the temperature of 5 and 10 wt % weight loss. Temperature for the maximum weight loss rate (T_{max}) in nitrogen was also measured at a heating rate of 20°C min^{-1} . Char yield (C_y) was calculated as the percentage of solid residue after heating from 200 to 800°C in flowing nitrogen. The glass transition temperature (T_g) was determined with a Mettler DSC822 DSC in flowing nitrogen at a heating rate of 10°C min^{-1} from 50 to 400°C. WAXD was performed at room temperature on a Shimadzu XRD-6000 automatic X-ray diffractometer with Ni-filtered Cu K_α radiation. The rotated velocity of the goniometry was 4° min^{-1} .

RESULTS AND DISCUSSION

Synthesis of PAEK copolymers

Several PAEK copolymers with different compositions were prepared by a modest two steps polycondensation reaction, as depicted in Scheme 1. The molecular weights (\bar{M}_n s), which were measured in chloroform by GPC or by ^{19}F NMR¹⁴ in concentrated sulfuric acid according to their solubilities, the yields and weight loss fractions were listed in Table I. It can be seen from Table I that the \bar{M}_n values of PAEK copolymers ranged from 6700 to 71,000 as phthalazinone content increased from 10 to 90 mol %. The resulting copolymers were fiber or powder like and

TABLE I
The Compositions and Physical Properties of PAEK Copolymers

Copolymers	Copolymer composition DHPZ/HQ	Yield (%)	Color	\bar{M}_n^a	MDI ^b	Weight loss ^c (%)
PAEK19	10/90	90	Yellow	6,700 ^d	– ^e	0.82
PAEK28	20/80	90	Yellow	7,500 ^d	–	0.71
PAEK37	30/70	90	Yellow	8,200 ^d	–	0.55
PAEK46	40/60	90	White	9,800 ^d	–	1.38
PAEK55	50/50	90	White	11,000 ^d	–	1.42
PAEK64	60/40	93	White	56,000	2.01	1.01 ^f
PAEK73	70/30	93	White	71,000	2.63	0.76 ^f
PAEK82	80/20	93	White	29,000	3.95	0.67 ^f
PAEK91	90/10	93	White	27,000	2.45	0.31 ^f

^a Detected in chloroform by GPC.

^b Molecular weight distribution index.

^c Determined by measuring the residual polymers extracted with chloroform.

^d Measured in concentrated sulfuric acid by ^{19}F NMR.

^e Not tested.

^f Determined by measuring the polymers precipitated from chloroform.

their color ranged from white to yellow. The fractions of weight loss of these copolymers, which were extracted with chloroform were all below 1.5 wt % and the yields were all higher than 90 wt %.

The \bar{M}_n values of PAEK64-PAEK91, which were measured in chloroform by GPC varied from 27,000 to 71,000. However, the maximum \bar{M}_n value, which was examined in concentrated sulfuric acid by ^{19}F NMR could just reached 11,000 and the lowest value was 6,700 among PAEK55-PAEK19 (Table I). This indicated the crystallization effect of PEEKK segment that would lead to the precipitating of PAEK copolymers from sulfolane solution prior to the formation of high molecular weight products. Consequently, the results show that the \bar{M}_n s of these copolymers increased as phthalazinone content rose in the main chain of these copolymers and should be attributed to the crank and twisted noncoplanar structure of phthalazinone moieties, which can improve the solubility of these copolymers in this reaction system.

The resulting PAEK copolymers were also extracted with chloroform, which was a good solvent for PPEKK,⁷ but not for PEEKK. The fractions of weight loss of PAEK copolymers after extraction were all below 1.5 wt %. Moreover, the results show that there was only one single T_g value for all of the PAEK copolymers from the DSC determination in Figure 4 and suggested that the polymers obtained should be copolymers of PPEKK and PEEKK rather than blends of two components. The structures of these resulting PAEK copolymers were also confirmed by the means of H H cosy NMR, ^1H NMR, and FTIR spectroscopy. Figure 1 showed the H H cosy NMR spectrum of PAEK82, the chemical shift

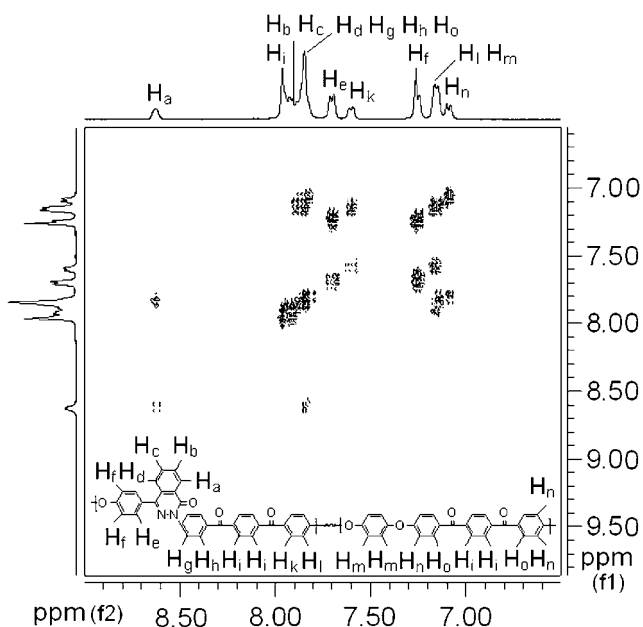


Figure 1 H-H cosy NMR spectrum of PAEK82.

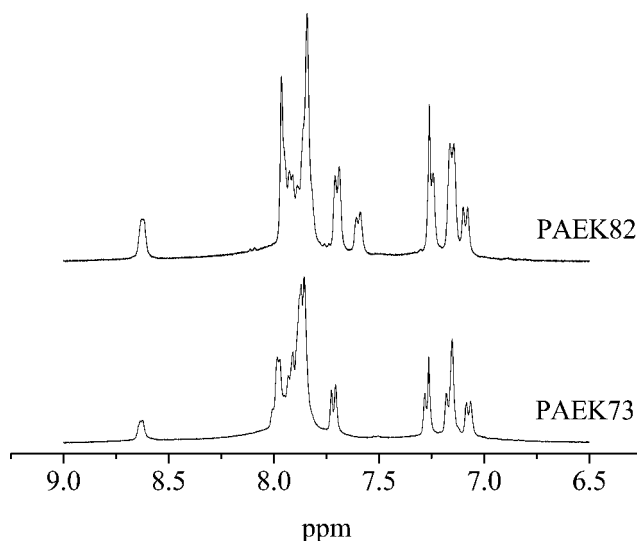


Figure 2 ^1H NMR spectra of PAEK82 and PAEK73.

assignments of relative protons, which were also listed in Figure 1 indicating the structure of PAEK82 as shown in Scheme 1. The comparison of ^1H NMR spectra for PAEK82 and PAEK 73 were depicted in Figure 2. A fact that the protons for PAEK82 and PAEK73 (in $\delta = 7.8\text{--}8.2$ ppm region) could not be separated clearly indicated that the sequences in the polymers are somewhat "short block" or "random." The FT-IR spectra of PAEK19, PAEK28, PAEK46, and PAEK82 were demonstrated in Figure 3. All of the PAEK copolymers showed no absorption bands in the $3200\text{--}3500\text{ cm}^{-1}$ region indicating the absence of $-\text{OH}$ or $-\text{NH}$ groups. And all of the IR spectra of PAEK copolymers showed the characteristic absorption bands near 1650 cm^{-1} (versus, $\nu\text{C}=\text{O}$), 1600 cm^{-1} , 1495 cm^{-1} (s, Ar stretching), 1240 cm^{-1} (versus, $\nu\text{C}-\text{O}-\text{C}$) and 1112 cm^{-1} (s, $\nu\text{N}-\text{N}$). The

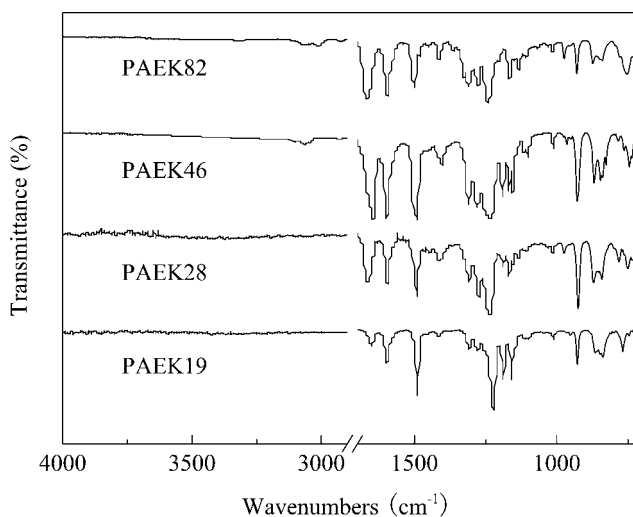


Figure 3 FTIR spectra of PAEK copolymers.

results of the IR analyses for these copolymers were in good agreement with the supposed compositions.

Polymer solubility

The solubility of PAEK copolymers was examined in various solvents at 25°C for 12 h by dissolving 50.0 mg of copolymers in 1 mL of solvent (5.0 w/v %), and the results were presented in Table II. It was observed from Table II that the solubility of PAEK copolymers was improved gradually as phthalazinone content became more in the main chain, such as PAEK46 and PAEK55 could be partially soluble in *N*-Methyl-2-pyrrolidinone (NMP), nitrobenzene (NB), 1,1,2,2-tetrachloroethane (TCE), and chloroform. PAEK copolymers with phthalazinone content more than 60 mol % in the backbone could be totally soluble in NMP, NB, TCE, chloroform and partially soluble in *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), and tetrahydrofuran (THF). Nevertheless, pure PEEKK,⁴⁻⁶ PAEK19, PAEK28, and PAEK37 were insoluble in all organic solvents except for concentrated sulfuric acid. The improved solubility of PAEK copolymers could be ascribed to the crank and twisted noncoplanar phthalazinone structure and the flexible ether linkages, which help to enlarge the average intermolecular distance of these copolymers and enable solvent molecules to diffuse easily into the copolymer chains.¹⁵

Thermal stability

The T_g and T_m of PAEK copolymers

The glass transition temperatures (T_g) and crystalline melting temperatures (T_m) of PAEK copolymers were evaluated by DSC, which were conducted at a heat-

ing rate of 10°C min⁻¹ in nitrogen from 50 to 400°C. The DSC curves of four typical PAEK copolymers were described in Figure 4, and the T_g and T_m values for the first and second scans and the calculated values from Fox equation¹⁶ were given in Table III.

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} \quad (1)$$

It could be seen from Figure 4 that the copolymers with different phthalazinone contents showed single T_g value. The T_g values for the copolymers were shifted to higher temperatures and the T_m values were shifted to lower temperatures as the phthalazinone content increased. The T_g values ranged from 168 to 235°C when the content of phthalazinone grew from 10 to 90 mol % in the main chain (Table III). The relationship between T_g values and phthalazinone content of PAEK copolymers were shown in Figure 5. The rule of random copolymers was created from the calculated T_g values, which were obtained from Fox Equation. Where T_{g1} and T_{g2} stand for the T_g values of PEEKK (T_{g1} , 162°C⁴) and PPEKK (T_{g2} , 245°C⁷), respectively. And W_1 , W_2 denote the corresponding weight fractions of the PEEKK and PPEKK segments in the copolymers. It was obvious that the variation of T_g curves with phthalazinone molar content approximately fitted the rule of random copolymers, especially for the second scan curve. These relatively higher T_g values in comparison with the T_g value of PEEKK (162°C) were also because of the introduction of phthalazinone structure in the backbone, which hindered the movement of the main chains,¹⁵ and the relatively high \bar{M}_n s (6,700–71,000) of these copolymers.

Almost all of the PAEK copolymers possessed a T_m value except PAEK91, although they (expressed

TABLE II
Solubilities of PAEK Copolymers

Copolymers	Solubility ^a								
	CHCl ₃	NMP	NB	TCE	DMAc	DMF	THF	DMSO	Conc. H ₂ SO ₄
PEEKK ^b	–	–	–	–	–	–	–	–	+
PAEK19	–	–	–	–	–	–	–	–	+
PAEK28	–	–	–	–	–	–	–	–	+
PAEK37	–	–	–	–	–	–	–	–	+
PAEK46	±	±	±	±	–	–	–	–	+
PAEK55	±	±	±	±	–	–	–	–	+
PAEK64	+	+	+	+	±	±	±	–	+
PAEK73	+	+	+	+	±	±	±	–	+
PAEK82	+	+	+	+	±	±	±	–	+
PAEK91	+	+	+	+	±	±	±	–	+
PPEKK ^c	+	+	+	+	±	±	±	–	+

^a Tested with 50 mg of the polymers in 1 ml of the solvent: +, totally soluble at 25°C for 12 h; ±, partially soluble at 25°C for 12 h; –, insoluble at 25°C for 12 h.

^b From Refs. 4 and 5.

^c From Ref. 7.

TABLE III
The T_g and T_m Values of PAEK Copolymers

Copolymers	T_g (°C) ^a	T_g (°C) ^b	T_g (°C) ^c	T_m (°C) ^a	ΔH (J g ⁻¹) ^a	T_m (°C) ^b	ΔH (J g ⁻¹) ^b
PEEK ^d	162	162	162 (T_{g1})	362	46.7	362	46.7
PAEK19	171	168	169	355	38.2	352	37.0
PAEK28	182	179	177	347	30.1	344	28.8
PAEK37	192	188	185	338	26.4	336	24.5
PAEK46	199	195	193	327	22.3	323	20.0
PAEK55	202	200	201	313	12.9	309	10.7
PAEK64	207	208	209	297	8.5	293	5.9
PAEK73	214	216	218	288	0.3	285	0.1
PAEK82	222	224	227	292	0.1	290	0.1
PAEK91	233	235	236	- ^e	-	-	-
PPEKK ^f	245	245	245 (T_{g2})	- ^g	-	-	-

^a Values of the first scan from DSC measurements conducted at a heating rate of 10°C min⁻¹ in nitrogen.

^b Values of the second scan from DSC measurements conducted at a heating rate of 10°C min⁻¹ in nitrogen.

^c Calculated from Fox Equation.

^d From Refs. 4 and 17.

^e No obvious peak was detected.

^f From Ref. 7.

^g Not referred in Ref. 7.

by ΔH) could not be detected (PAEK 82 in Fig. 4) when the content of phthalazinone was more than 60 mol %, and the T_m values for the second scan varied from 352 to 285°C as phthalazinone content changed from 10 to 80 mol % in Table III.

The results presented above suggested that the incorporating of phthalazinone structure in the backbone cumbered the close packing of the crystal unit cells that caused the enthalpy (ΔH) to reduce and disordered the regularity of the main chains that induced the increase of entropy (ΔS); both of the two factors led to the decrease of T_m according to eq. (2).⁴

$$T_m = \frac{\Delta H}{\Delta S} \quad (2)$$

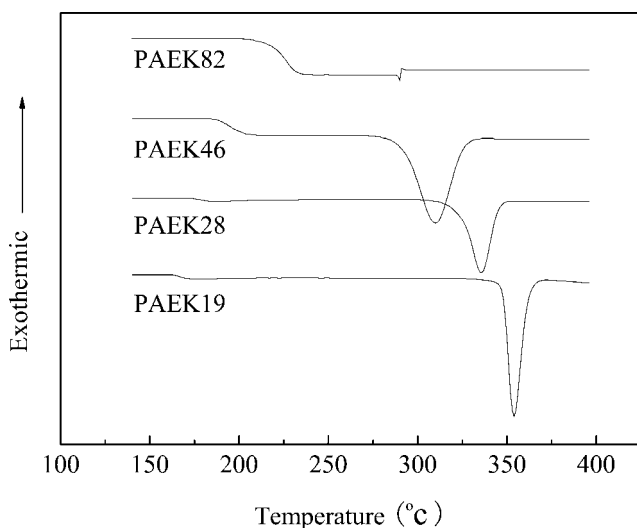


Figure 4 The second scanning DSC curves of PAEK copolymers annealed at 260°C for 5 h.

It is considered that the high T_g values and the relatively low T_m values existed concurrently would be of significance to the melt processing technology and high temperature applications. Moreover, the improved solubility of PAEK copolymers will make the solution processing technology of phthalazinone-containing PAEKs facile and enlarge the application fields in fiber-reinforced composites, high performance coatings, and cable insulators etc. The further efforts in this aspect are in progress by our team.

TGA and DGT analyses of PAEK copolymers

The weight loss temperature (T_d) and the maximum weight loss rate (T_{max}) in nitrogen were investigated by the means of TGA and DTG at a heating rate of

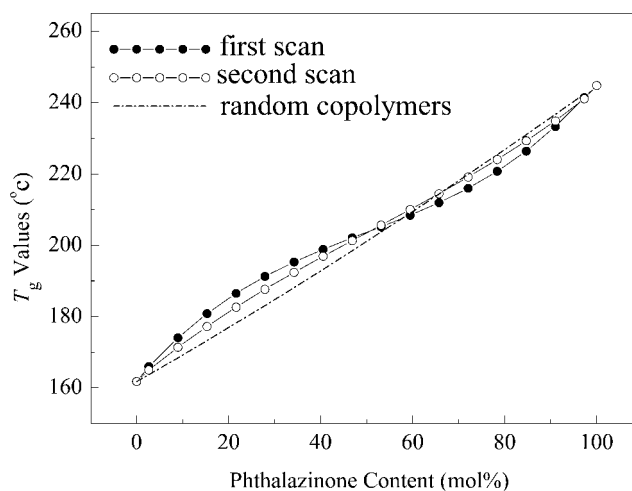


Figure 5 The relationship between T_g values and phthalazinone content of PAEK copolymers.

TABLE IV
The Weight Loss Temperatures and Char Yields of PAEK Copolymers

Copolymers	$T_{5\%}$ (°C) ^a	$T_{10\%}$ (°C) ^b	T_{\max} (°C) ^c	C_y (%) ^d
PEKK ^e	540 ^f	— ^g	—	—
PAEK19	538	550	562	62
PAEK28	530	547	565	60
PAEK37	528	546	563	59
PAEK46	524	544	562	61
PAEK55	520	540	560	58
PAEK64	515	535	557	59
PAEK73	517	539	559	58
PAEK82	519	541	563	56
PAEK91	510	532	560	60
PPEKK ^h	507	—	—	—

^a Temperature for 5% weight loss in nitrogen, heating rate of 20°C min⁻¹.

^b Temperature for 10% weight loss in nitrogen, heating rate of 20°C min⁻¹.

^c Temperature for the maximum weight loss rate in nitrogen, heating rate of 20°C min⁻¹.

^d Char yield calculated as the percentage of solid residue after heating from 200 to 800°C in nitrogen.

^e From Ref. 5.

^f Temperature for 2.5% weight loss in nitrogen, heating rate of 20°C min⁻¹ from Ref. 5.

^g Not referred in Refs. 5 and 7.

^h From Ref. 7.

20°C min⁻¹ in nitrogen. The results are summarized in Table IV, and the TGA and DTG curves in nitrogen of typical PAEK copolymers were shown in Figure 6.

The weight loss temperatures (T_d) of PAEK copolymers were in the range of 510–538°C [$T_{d5\%}$ (weight loss percent) Table IV] and 532–550°C ($T_{d10\%}$ Table IV) which almost kept the same heat resistance as pure PEEKK ($T_{d2.5\%} = 540^\circ\text{C}$ ⁵) and a little higher than that of pure PPEKK ($T_{d5\%} = 507^\circ\text{C}$ ⁷). Accordingly, the thermal stabilities of these PAEK copolymers were still excellent.

As illustrated in Figure 6, when phthalazinone content kept a growing trend from 10 to 80 mol % in the main chains of these copolymers, the TGA curves declined slightly and the temperatures for the maximum of a single step of weight loss rate were also varied slightly. Temperatures of T_{\max} in nitrogen ranged from 557 to 565°C, and the char yields (C_y) of PAEK copolymers were in the range of 56–62 wt % in Table IV. These resultant data suggested that PAEK copolymers in this study possessed excellent thermal stability.

Crystallinity of PAEK copolymers

The crystallinity of PAEK copolymers, which were annealed at 260°C for 5 h, was characterized by the mean of WAXD. Although a few of crystal structures of PEEK and PEEKK have been reported,^{17–24} so far there is no report concerning the cell parameters,

crystal unit cell volume (V), crystal unit cell density (ρ_c), and degree of crystallinity (X_c) of phthalazinone-containing PAEK polymer family. And to the best of our knowledge, the crystal unit cell parameters of PAEK19, PAEK28, and PAEK46 were measured and discussed here for the first time. The representative cell parameters' measurement of PAEK46 was depicted as follows.

The WAXD pattern of the isothermally crystallized PAEK46 at 260°C for 5 h was shown in Figure 7(C). The crystallographic planes, the 2 θ degrees, the observed and calculated interplanar spacing (d), and relative intensities (I/I_0) of PAEK46 are given in Table V. The 20 independent reflections were recorded, and with the help of trail and error method, all of them could be satisfactorily indexed by assuming an orthorhombic unit cell of the lattice dimensions $a = 7.99 \text{ \AA}$, $b = 6.14 \text{ \AA}$ and $c = 10.19 \text{ \AA}$ (Table V) according to eq. (3).^{19,25}

$$\frac{1}{d_{hkl}^2} = \frac{a^2}{h^2} + \frac{b^2}{k^2} + \frac{c^2}{l^2} \quad (3)$$

The crystal density, calculated by presuming that one unit cell contained two PEEKK chains, was 1.302 g cm⁻³ correlated acceptably with amorphous and semicrystalline densities of 1.22 and 1.25 g cm⁻³, respectively.¹⁹

The measurement density together with the crystallographic data did establish the model of two chains per unit cell. Therefore, depending on the packing model of PEEKK molecular chain [Fig. 8(A)], a packing model of PEEKK segment in PAEK46 was proposed as shown in Figure 8(B). There was one

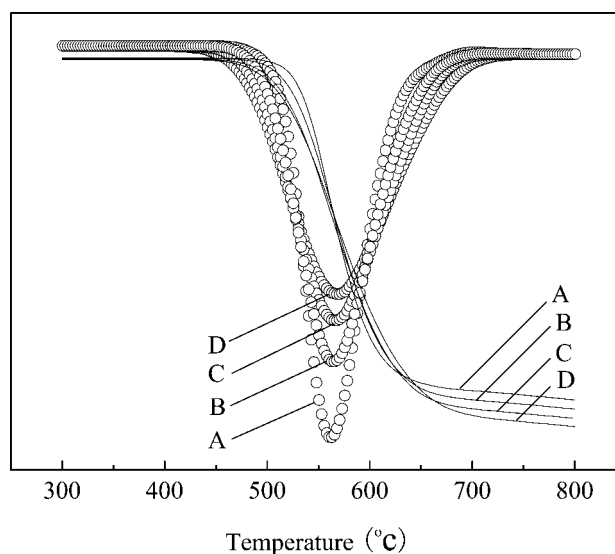


Figure 6 TGA and DTG curves of PAEK copolymers: (A) PAEK19, (B) PAEK28, (C) PAEK46, (D) PAEK82.

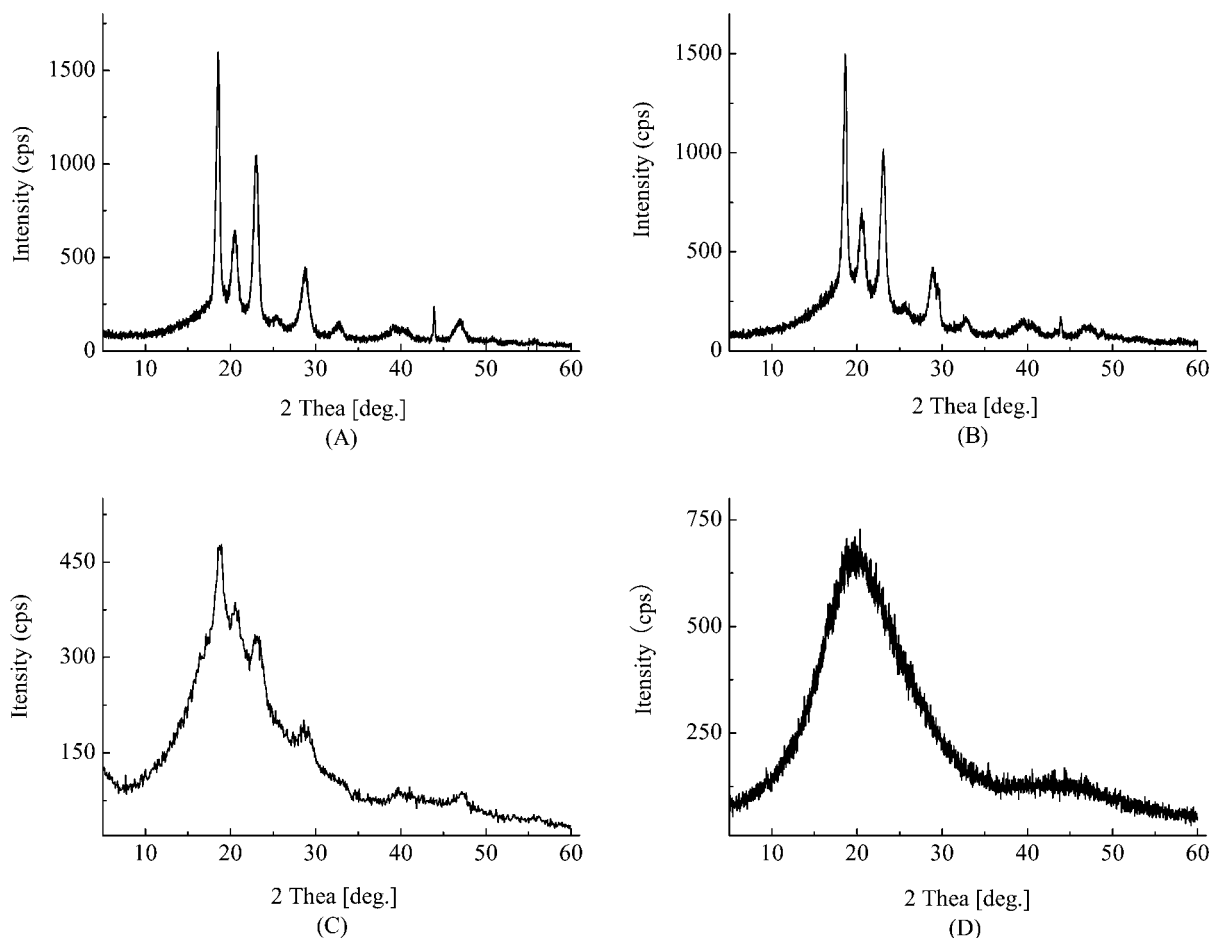


Figure 7 WAXD diffractograms of PAEK copolymers annealed at 260°C for 5 h: (A) PAEK19, (B) PAEK28, (C) PAEK46, (D) PAEK82.

TABLE V
The Indices of Crystallographic Planes and Their Relative Diffraction Intensities of PAEK46

No.	hkl	2θ (°)	d_o (Å) ^a	d_c (Å) ^b	I/I_o ^c
1	002	17.39	5.07	5.09	37
2	110	18.21	4.89	4.87	100
3	111	20.21	4.40	4.39	65
4	200	22.28	3.99	3.99	74
5	012	22.59	3.92	3.92	70
6	112	25.30	3.52	3.52	30
7	211	27.94	3.19	3.18	46
8	020	29.09	3.07	3.07	24
9	212	31.97	2.80	2.80	21
10	113	32.12	2.78	2.78	19
11	121	32.39	2.76	2.76	20
12	022	34.39	2.65	2.63	15
13	122	35.91	2.50	2.50	14
14	220	36.89	2.43	2.43	15
15	213	37.75	2.39	2.38	16
16	302	38.02	2.36	2.36	19
17	114	40.00	2.26	2.26	18
18	214	44.71	2.02	2.02	14
19	321	46.01	1.97	1.97	15
20	024	46.10	1.96	1.96	23

^a The values of observed interplanar spacing.

^b The values of calculated interplanar spacing.

^c The values of relative intensities.

chemical repeat unit (or two crystallographic repeat units) in the chain direction of the unit cell. And taking these results into account, it could be presumed that PPEKK segments were not in the crystal unit cell of the copolymers, but in the noncrystalline phase between the crystalline lamella.^{17–24} The systematic absence of the reflections $hk0$ with $h+k = \text{odd}$, $0kl$ with $k = \text{odd}$ and $h0l$ with $l = \text{odd}$ led us to the spacing group $Pbcn-D_{2h}$.^{19,25}

Every copolymer except for PAEK82 in Figure 7 displayed four main diffraction peaks in their WAXD patterns. Compared with the WAXD data of PEEKK and its copolymers reported previously,^{4,5,8–15,17–24,26,27} the average diffraction peak positions of PAEK copolymers at 18°, 20°, 23°, and 29° were assigned to 110, 111, 200, 211 reflections.⁴ The diffraction peak intensities of PAEK19, PAEK28, and PAEK46 reduced gradually as the content of phthalazinone in the main chain ranged from 10 to 40 mol % in Figure 7. The evidences in Figure 7(D) show that obvious diffraction peaks could not be examined for PAEK82 at the same measurement condition indicated that the polymer showed an amorphous phase,

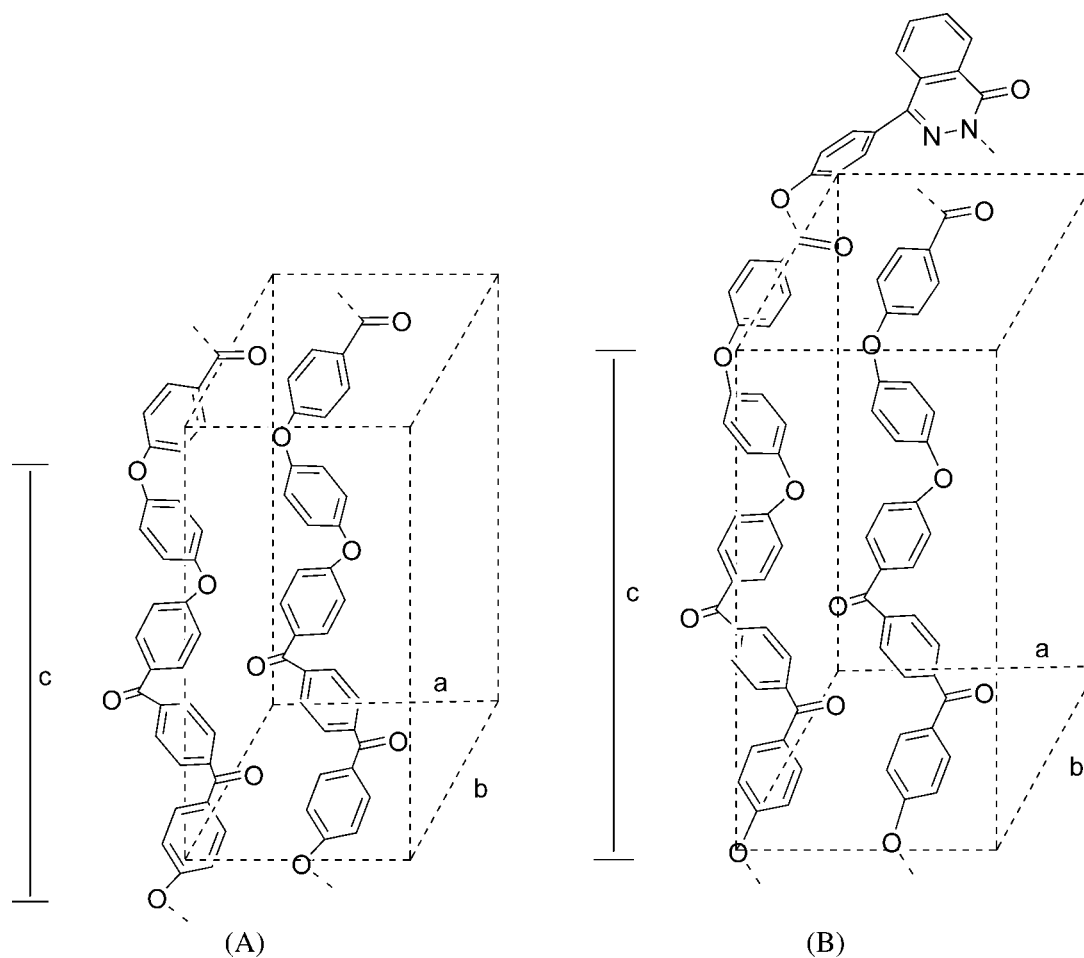


Figure 8 Stereodiagram of the unit cell of PEEKK (A) and PAEK46 (B).

and the melting peak in Figure 4 for PAEK82 maybe the reason of crystallization for PAEK82 above its T_g during the DSC scan. A noticeable result is that phthalazinone structure in the backbones of these copolymers may cumber the close packing of the copolymer chains and decrease the degree of crystallinity.

The cell parameters, V , ρ_c , and X_c values of PAEK19-PAEK46 were collected in Table VI for a comparison, together with the data of pure PEEKK.¹⁸ A comparison of cell parameters (a , b , c), V , and ρ_c for these five polymers in Table VI indicated that the introduction of phthalazinone structure into the main chains had a obvious effect on these values. The

TABLE VI
Cell Parameters and Degrees of Crystallinities of PAEK Copolymers Determined From WAXD Pattern of the Powders

Copolymer	a (Å)	b (Å)	c (Å)	V (Å ³)	M^a (g mol ⁻¹)	ρ_c^b (g cm ⁻³)	X_c (%) ^c (via DSC)	X_c (%) ^d (via WAXD)
PEKK ^e	7.75	6.00	10.10	470	392	1.385	37.70	37.50
PAEK19	7.82	6.04	10.13	478	392	1.362	29.81	28.46
PAEK28	7.91	6.09	10.16	489	392	1.331	23.22	22.91
PAEK46	7.99	6.14	10.19	500	392	1.302	16.14	15.86
PAEK82	- ^f	-	-	-	-	-	0.08	-

^a The molecular weight of molecular repeating unit in the crystal.

^b Calculated by the equation $\rho_c = ZM/NV$, where Z is the molecular chain number through the crystal unit cell (in this case is 2), N is Avogadro's constant.^{17,24}

^c Calculated by the equation $X_c = \Delta H/\Delta H_f \times 100\%$, where ΔH is the heat fusion of the copolymer determined by DSC, ΔH_f is the heat of fusion of 100% crystalline PEEKK ($\Delta H_f = 124 \text{ J g}^{-1}$).¹⁷

^d Calculated from the results of WAXD.¹⁹

^e From Ref. 17.

^f No obvious peaks were detected.

increases of 0.07–0.09 Å for *a* axis length, 0.04–0.05 Å for *b* axis length, and 0.03 Å for *c* axis length together with the increase of 8–11 Å³ for *V* were observed (Table VI) as the content of phthalazinone varied from 0 to 40 mol % in these copolymers. Compared with the increases of *a*, *b*, *c* axes lengths and *V*, the values of ρ_c were lowered by about 0.023, 0.030, and 0.029 g cm⁻³ for PAEK19-PAEK46, respectively. The values of X_c (via WAXD) for PAEK19, PAEK28, and PAEK46 were also lowered by 23% averagely.

It could be predicted that for phthalazinone structure of large volume a twisted and noncoplanar configuration should be sterically more bulky than a HQ structure of coplanar configuration in the backbone of PAEK copolymers as shown in Figure 8. It is noteworthy that PAEK copolymers with phthalazinone structure in the main chains feature a more bulky configuration in the noncrystalline phase between the crystalline lamella, implying that the average intermolecular distance is enlarged.

CONCLUSIONS

A series of organic soluble semicrystalline PAEK copolymers containing phthalazinone moieties and ether linkages were prepared by a modest two steps polycondensation reaction. These resultant copolymers exhibited higher T_g values than that of PEEKK, and this trend kept growing with the increase of phthalazinone content. Moreover, these examined T_g values approximately followed the curves, which were originated from Fox Equation. Meanwhile, the crystalline melting temperatures (T_m) and degree of crystallinity (X_c) showed the opposite trend in contrast to these T_g values. The TGA and DTG determinations indicated that these copolymers possessed excellent thermal stabilities. Introducing ether linkages and bulky, crank and twisted noncoplanar phthalazinone structure in the main chains increased the solubility greatly in some common polar organic solvents. It is for the first time to measure the cell parameters of phthalazinone-containing PAEK copolymers, which were seldom available on published papers and calculate the values of *V*, ρ_c , and X_c . Evidences from the variations of cell parameters, which increased in direct proportion with the increase of phthalazinone content in these copolymers, suggested that incorporating phthalazinone moieties and ether linkage into the main chains could increase the intermolecular distance. Hence, the results show that the T_g values rose gradually with the increase of phthalazinone content in these copolymers' backbone

while the T_m values decreased evidently suggested that these positive properties on high temperature application and processing existed simultaneously together with the improved solubility in some common polar organic solvents would be precious references for the prospect of future applications for these PAEK copolymers.

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