

Crosslinkable poly(aryl ether ketone)s containing pendant phenylethynyl moieties: Synthesis, characterization and properties

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ABSTRACT

A novel phenylethynyl-contained bisphenol monomer, (2,5-dihydroxyphenyl)(4-(2-phenylethynyl)-phenyl)methanone (PEBP), has been synthesized and characterized. The resultant monomer was copolymerized with hydroquinone and 4,4'-difluorobenzophenone by means of an aromatic nucleophilic substitution reaction to provide a series of crosslinkable poly(aryl ether ketone)s containing pendant phenylethynyl moieties (PE-PAEKs). The solubility of PE-PAEKs tended to be improved with the increase in PEBP content. Wide-angle X-ray diffraction (WAXD) results showed that introduction of bulky pendant groups into molecular chains led to decrease in crystallinity. PE-PAEKs were successfully cured upon heating. Dynamic mechanical analysis (DMA) results indicated that the glass-transition temperature (T_g) of the cured PE-PAEKs was increased. Thermogravimetric analysis (TGA) results implied that the thermal stability of the cured PE-PAEKs was excellent.

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1. Introduction

High performance engineering plastics, poly(aryl ether ketone)s (PAEKs) have received considerable attention from industry and academy, due to their high mechanical properties, excellent thermooxidative stability and chemical resistance [1]. Two of the most prominent examples, poly(ether ether ketone) (PEEK) and poly(ether ketone) (PEK) have been used in a variety of applications such as aerospace, electronics and automobile [1].

However, due to their semicrystalline property, these polymers are insoluble in organic solvents at ambient temperature, except for strong acids [1–3]. Therefore, they cannot be processed by the casting method and require a high molding temperature resulted from their high melting temperature (around 340 °C) [1,3,4]. At the same time, the glass-transition temperature (T_g) of these polymers is low (around 140 °C), which leads to a low dimension stability [1,3,4].

Considerable efforts have been devoted for improving the processability and glass-transition temperature of PAEKs. It has been suggested that introduction of heterocyclic moieties, pendant groups and asymmetry structure onto the molecular chains of PAEKs could improve the processability and/or glass-transition temperature [1,3,5–9]. Crosslinkable PAEKs have also been

synthesized to improve the glass-transition temperature of PAEKs, for example, incorporation of crosslinkable groups into molecular chains [10–12], and ring-opening polymerization and crosslinking of macrocycle aryl ether ketone [13,14], and irradiation crosslinking [15–17]. Crosslinkable groups, such as styrene groups, propargyl ether groups and benzocyclobutene groups have been incorporated into the molecular chains of PAEKs [10–12]. However, for high temperature applications, phenylethynyl groups are often preferred [18].

Phenylethynyl groups can offer a combination of properties not available in other crosslinkable groups, such as long shelf life at room temperature, wide processing window for the uncured material, and excellent mechanical properties for the cured material [18,19]. Although, previous studies have reported the synthesis and properties of PAEKs containing phenylethynyl moieties, improvement of the glass-transition temperature afforded by the cured PAEKs containing phenylethynyl moieties was limited [20–23]. It implies that the relationship between the structure and properties of PAEKs containing phenylethynyl moieties should be further investigated. Therefore, our research focuses on the molecular design and synthesis of crosslinkable PAEK with higher T_g and good processability, usually used as a matrix for fiber reinforced composites.

In this paper, we reported the synthesis and characterization of a novel phenylethynyl-contained bisphenol monomer (PEBP). The phenylethynyl-contained bisphenol monomer was copolymerized with hydroquinone and 4,4'-difluorobenzophenone through an aromatic nucleophilic substitution reaction to afford a series of

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crosslinkable poly(aryl ether ketone)s containing pendant phenylethynyl moieties (PE-PAEKs). The solubility of the uncured PE-PAEKs was investigated and the crystallinity was studied by wide-angle X-ray diffraction (WAXD). The curing reaction of PE-PAEKs was confirmed by Fourier transform infrared (FTIR). The glass-transition temperature of the cured PE-PAEKs was investigated by dynamic mechanical analysis (DMA). The thermal stability of the uncured and cured PE-PAEKs was studied by thermogravimetric analysis (TGA).

2. Experimental section

2.1. Materials

Hydroquinone was purchased from Beijing Chemical Reagent Corporation (China) and used without further purification. 4,4'-Difluorobenzophenone was obtained from Yanji Chemical Plant (China) and distilled before use. Phenylacetylene, dichlorobis(triphenyl phosphine)palladium(II) and copper(I) iodide were obtained from Aldrich Chemical Co. and used as received. Triethylamine and 1,2-dichloroethane were dried over calcium hydride and distilled before use. Tetrahydrofuran was dried on sodium and distilled before use. Other reagents were purchased from Beijing Chemical Reagent Corporation (China) and used as received.

2.2. Monomer synthesis

2.2.1. Synthesis of 1,4-diethoxybenzene (**1**)

Into a three-necked round-bottomed flask equipped with a magnetic stirrer, a condenser and a dropping funnel, hydroquinone (25.00 g, 0.23 mol) was dissolved in ethanol (200 ml). KOH (30.51 g, 0.54 mol) was added to the reaction solution slowly. Then bromoethane (74.22 g, 0.68 mol) was added to the system in drops. The reaction mixture was heated to reflux and maintained for 6 h. The reaction solution was filtrated to remove the salts, and the filtrate was collected and rotary-evaporated at 50 °C to remove the solvent. The residue was recrystallized from ethanol/water (1/1, v/v). After dried under vacuum for 24 h at 50 °C, 1,4-diethoxybenzene (**1**) was obtained as a white solid (Yield: 84%). Mass spectrum (*m/e*): 166. ¹H NMR (200 MHz, CDCl₃, δ, ppm): 1.34–1.41 (t, 6H), 3.91–4.02 (m, 4H), 6.81 (s, 4H).

2.2.2. Synthesis of (4-bromophenyl)(2,5-dihydroxyphenyl)methanone (**3**)

Into a 250 ml one-necked round-bottomed flask equipped with a magnetic stirrer, 4-bromobenzoic acid (10.00 g, 0.050 mol) was dissolved in thionyl chloride (100 ml) containing DMF (3 drops). The reaction mixture was gently heated to reflux and maintained for 3 h. Excess amount of thionyl chloride was distilled off by rotary-evaporator. 4-Bromobenzoyl chloride was obtained as a white needle crystal.

Into a 250 ml three-necked round-bottomed flask equipped with a magnetic stirrer, an argon inlet and outlet, and a dropping funnel, anhydrous aluminum chloride (15.19 g, 0.11 mol) and 1,4-diethoxybenzene (**1**) (13.61 g, 0.082 mol) were dissolved in 1,2-dichloroethane (130 ml). After the reaction mixture was cooled to 5 °C in an ice bath, a solution of 4-bromobenzoyl chloride (10.00 g, 0.046 mol) in 1,2-dichloroethane (50 ml) was added in drops for 0.5 h. The reaction mixture was allowed to room temperature. After 12 h of stirring, the reaction mixture was poured into 5% hydrochloric acid. The organic layer was extracted by dichloromethane, and washed with deionized water for three times, and rotary-evaporated to dryness. A yellowish solid residue was obtained.

Into a 500 ml three-necked round-bottomed flask equipped with a magnetic stirrer and an argon inlet and outlet, the obtained yellowish solid product (25.49 g) was dissolved in acetic acid

(200 ml) containing HBr (50 ml). The reaction mixture was heated to reflux and maintained for 48 h. Then, the reaction mixture was distilled by rotary-evaporator. The resulting solid residue was dissolved in ethanol and precipitated in deionized water for three times. After recrystallized in toluene and dried under vacuum for 24 h at 50 °C, (4-bromophenyl)(2,5-dihydroxyphenyl)methanone (**3**) was obtained as a yellowish solid (Yield: 57%). Mass spectrum (*m/e*): 292. ¹H NMR (200 MHz, CDCl₃, δ, ppm): 6.97–7.00 (d, 1H), 6.98–6.99 (d, 1H), 7.07–7.11 (dd, 1H), 7.56–7.68 (m, 4H), 4.50 (s, 1H), 11.42 (s, 1H).

2.2.3. Synthesis of (4-bromophenyl)(2,5-diacetoxyphenyl)methanone (**4**)

Into a 250 ml three-necked round-bottomed flask equipped with a magnetic stirrer and an argon inlet and outlet, (4-bromophenyl)(2,5-dihydroxyphenyl)methanone (**3**) (6.00 g, 0.021 mol) was dissolved in acetic anhydride (120 ml) containing H₂SO₄ (3 drops). The reaction mixture was heated to 60 °C, and maintained for 24 h. The reaction mixture was poured into deionized water. The resulting precipitate was filtrated and recrystallized from ethanol/water (1/1, v/v). After dried under vacuum for 24 h at 60 °C, (4-bromophenyl)(2,5-diacetoxyphenyl)methanone (**4**) was obtained as a white needle crystal (Yield: 96%). Mass spectrum (*m/e*): 376. ¹H NMR (200 MHz, CDCl₃, δ, ppm): 2.02 (s, 3H), 2.30 (s, 3H), 7.18–7.33 (m, 3H), 7.59–7.69 (m, 4H).

2.2.4. Synthesis of (2,5-dihydroxyphenyl)(4-(2-phenylethynyl)phenyl)methanone (**6**)

Into a 100 ml three-necked round-bottomed flask equipped with a magnetic stirrer, a condenser, a dropping funnel and an argon inlet, (4-bromophenyl)(2,5-diacetoxyphenyl)methanone (**4**) (3.00 g, 7.50 mmol), triphenylphosphine (0.099 g, 0.38 mmol), CuI (0.086 g, 0.38 mmol), dichlorobis(triphenyl phosphine)palladium(II) (0.26 g, 0.38 mmol) was dissolved in triethylamine (25 ml) and tetrahydrofuran (25 ml). Phenylacetylene (0.85 g, 8.30 mmol) dissolved in tetrahydrofuran (15 ml) was added in drops for 0.5 h. The reaction mixture was heated to reflux and maintained for 24 h. Then, the reaction mixture was cooled to room temperature and filtrated. The resulting filtrate was rotary-evaporated. And the residue was purified by flash column chromatography on silica (dichloromethane). Then (2,5-diacetoxyphenyl)(4-(2-phenylethynyl)phenyl)methanone (**5**) was obtained as a white crystal (Yield: 73%). Mass spectrum (*m/e*): 398. ¹H NMR (200 MHz, DMSO-*d*₆, δ, ppm): 1.92 (s, 3H), 2.28 (s, 3H), 7.35–7.49 (m, 6H), 7.58–7.65 (m, 2H), 7.73(s, 4H).

Into a 100 ml three-necked round-bottomed flask equipped with a magnetic stirrer, a condenser, a dropping funnel and an argon inlet and outlet, (2,5-Diacetoxyphenyl)(4-(2-phenylethynyl)phenyl)methanone (**5**) (4.00 g, 0.010 mol) was dissolved in ethanol (70 ml). Anhydrous potassium carbonate (6.93 g, 0.050 mol) dissolved in deionized water (10 ml) was added in drops. Then, the reaction mixture was heated to reflux and maintained for 6 h. The reaction mixture was poured to 5% hydrochloric acid. The resulting precipitate was collected by filtration. The yellowish solid was purified by flash column chromatography in silica (dichloromethane/ethyl acetate = 15:1). Then (2,5-dihydroxyphenyl)(4-(2-phenylethynyl)phenyl)methanone (**6**) was obtained as an carrot crystal (Yield: 71%). Mp [differential scanning calorimetry (DSC)]: 185 °C. Elemental analysis, Calcd. for C₂₁H₁₄O₃: C, 80.24%; H, 4.49%; O, 15.27%. Found: C, 80.14%; H, 4.40%; O, 15.46%. Mass spectrum (*m/e*): 314. ¹H NMR (400 MHz, DMSO-*d*₆, δ, ppm): 6.76 (d, ⁴J = 2.80 Hz, 1H), 6.83–6.85 (d, ³J = 8.77 Hz, 1H), 6.90–6.93 (dd, ³J = 8.79 Hz, ⁴J = 2.82 Hz, 1H), 7.45–7.46 (m, 3H), 7.60–7.62 (m, 2H), 7.69–7.76 (m, 4H), 9.12 (s, 1H), 9.80 (s, 1H). ¹³C NMR (100 MHz, DMSO-*d*₆, δ, ppm): 88.66, 92.08 (ethynyl), 115.61, 117.79, 121.14, 121.76, 124.00, 126.28, 128.81, 129.24, 129.47, 131.32, 131.53, 137.10,

149.61, 149.98 (phenyl) and 196.62 (carbonyl). FTIR (KBr, cm^{-1}): 3357 (O–H), 2218 ($\text{C}\equiv\text{C}$), 1630 ($\text{C}=\text{O}$), 1597, 1508, 1437 (phenyl).

2.3. Synthesis of poly(aryl ether ketone)s containing phenylethynyl moieties (PE-PAEKs)

Poly(aryl ether ketone)s containing pendant phenylethynyl moieties had been synthesized through an aromatic nucleophilic substitution reaction. A typical reaction procedure was depicted as follows.

Into a 100 ml three-necked round-bottomed flask equipped with a magnetic stirrer, a Dean-stark trap fitted with a condenser and an argon inlet and outlet, 4,4'-difluorobenzophenone (0.57 g, 2.60 mmol) was dissolved in DMAc (20 ml) and toluene (35 ml). Then, hydroquinone (0.055 g, 0.50 mmol) and PEBP (0.63 g, 2.00 mmol) was added. After the solids were dissolved, anhydrous potassium carbonate (0.76 g, 5.50 mmol) was added. The reaction mixture was heated to 145 °C and vigorously stirred until no more water was formed by azeotropic distillation. Toluene was then removed slowly as the reaction mixture was heated to 165 °C. The reaction temperature was maintained at 165 °C for 6 h. The reaction mixture was poured into 500 ml 10% hydrochloric acid. The resulting precipitate was filtrated and washed with hot water twice. The obtained polymer was Soxhlet-extracted with methanol for 48 h. The product was dried at 60 °C under vacuum for 48 h. Then the PAEK containing 80 mol% PEBP (relative to total bisphenols) was obtained as a gray powdered solid, which was denoted as PE-PAEK80 (Yield: 95%).

2.4. Thermal curing of poly(aryl ether ketone)s containing pendant phenylethynyl moieties

To investigate the thermal stability of the cured PE-PAEKs, PE-PAEKs were cured as follows.

PE-PAEKs were dissolved in CH_2Cl_2 at a concentration of 0.2 mg/ml. The solution was cast on a glass plate, and dried at ambient temperature. The polymer films obtained were cured at 370 °C for 1 h in an air oven.

To investigate the glass-transition temperature of the cured PE-PAEKs, glass fiber reinforced composites were prepared as follows.

PE-PAEKs were dissolved in DMF at a concentration of 4.0 mg/ml. Glass fiber cloth was dipped in the solution, and dried in a dry box containing concentrated H_2SO_4 as dry reagent at 40 °C for 48 h. The glass fiber cloth prepared was molded by heating to 300 °C for 10 min under pressure of 10 MPa and heating to 370 °C for 1 h under pressure of 15 MPa. Then the specimens (30 mm \times 10 mm \times 0.05 mm) were obtained.

2.5. Measurements

Nuclear magnetic resonance (NMR) spectra were obtained with a Bruker ARX-400 NMR spectrometer or a Varian YH200 NMR spectrometer using deuterated dimethyl sulfone (DMSO) or chloroform as the solvent with tetramethylsilane (TMS) as the internal reference. Elemental analysis was performed on a VARIO EL elemental analyzer. Mass spectrum was performed on a ZAB-HS gas chromatograph-mass spectrometer. Fourier transform infrared (FTIR) measurements were conducted on a Bio-Rad FTS-65A Fourier transform infrared spectrometer at room temperature (25 °C). The solid samples were embedded in KBr disks. In all cases, 32 scans at a resolution of 2 cm^{-1} were used to record the spectra. Gel permeation chromatogram (GPC) analysis was performed on a Waters 2410 instrument with tetrahydrofuran (THF) as eluent and monodisperse polystyrene as standards. Wide-angle X-ray diffraction (WAXD) measurements were carried out at room temperature (25 °C) on powdered samples employing a Philips

X'pertpro X-ray diffractometer with Cu K_α radiation ($\lambda = 0.154$ nm). Specimens were scanned from 10° to 35° with a scan speed of 0.2°/min. Differential scanning calorimetry (DSC) analysis were performed on powdered samples using TA Q100 differential scanning calorimeter at a heating rate of 10°/min under nitrogen atmosphere. Glass-transition temperature of uncured PE-PAEKs was reported as temperature at the middle of the thermal transitions for the second scan. Dynamic mechanical analysis (DMA) were performed from 25 °C to 400 °C using Netzsch DMA 242C instrument in the three-point bending mode at a heating rate of 5 °C/min and at a load frequency of 1 Hz in a nitrogen atmosphere. The loss factor, $\tan \delta$ was obtained as a function of temperature and the peak temperature of $\tan \delta$ was defined as T_g of the cured PE-PAEKs. A TA Q600 SDT thermogravimetric analyzer was used to investigate the thermal stability of the uncured and cured PE-PAEKs. All the thermal analyses were conducted in nitrogen atmosphere from 25 °C to 800 °C at a heating rate of 10 °C/min. The thermal degradation temperature was taken as the onset temperature at which 5 wt% weight loss occurred.

3. Results and discussion

3.1. Synthesis and characterization of monomer

The synthesis of the phenylethynyl-contained bisphenol monomer was conducted according to the procedure shown in Fig. 1.

The sequence started with hydroquinone which was treated with bromoethane to afford 1,4-diethoxybenzene (**1**). Then, Friedel–Craft reaction of **1** with 4-bromobenzoyl chloride in the presence of anhydrous aluminum chloride yielded (4-bromophenyl)(2,5-diethoxyphenyl)methanone (**2**). Then, **2** was treated with acetic acid and HBr to afford (4-bromophenyl)(2,5-dihydroxyphenyl)methanone (**3**), which was esterified in acetic anhydride containing H_2SO_4 to provide (4-bromophenyl)(2,5-diacetoxyphenyl)methanone (**4**). Compound **4** was coupled with phenylacetylene with Pd(0)/Cu(I) as a catalyst through a Sonogashira coupling reaction to afford (2,5-diacetoxyphenyl)(4-(2-phenylethynyl)phenyl)methanone (**5**). Finally, **5** was converted to (2,5-dihydroxyphenyl)(4-(2-phenylethynyl)phenyl)methanone (**6**) (PEBP) by hydrolysis in ethanol/water.

The identity and purity of the resultant phenylethynyl-contained bisphenol monomer (PEBP) were ascertained by convenient organic characterization prior to polymerization reaction, including FTIR, ^1H and ^{13}C NMR spectroscopy and elemental analysis.

The FTIR spectrum of the monomer is shown in Fig. 2. The spectrum showed the characteristic band of ethynyl groups at 2218 cm^{-1} and characteristic band of hydroxyl groups at 3357 cm^{-1} . Shown in Fig. 3 is ^1H NMR spectrum of the monomer and the assignments of the peaks are also given. The results of elemental analysis of the monomer were in accordance with those calculated values.

3.2. Synthesis and characterization of polymers

To obtain crosslinkable PAEK, the phenylethynyl-contained bisphenol monomer (PEBP) was copolymerized with hydroquinone (HQ) and 4,4'-difluorobenzophenone (DF) to afford poly(aryl ether ketone)s containing pendant phenylethynyl moieties through an aromatic nucleophilic substitution reaction (Fig. 4). It has been noted that the terminal groups could affect the thermal stability of the polymers [24]. In order to ensure the most of the chains were fluorine terminated, the molar ratio of bisphenol monomers and bis-fluoro monomer was maintained at 1:1.05. While the molar ratio of hydroquinone and PEBP was varied, as shown in Table 1, a series of PAEKs containing pendant phenylethynyl moieties were synthesized.

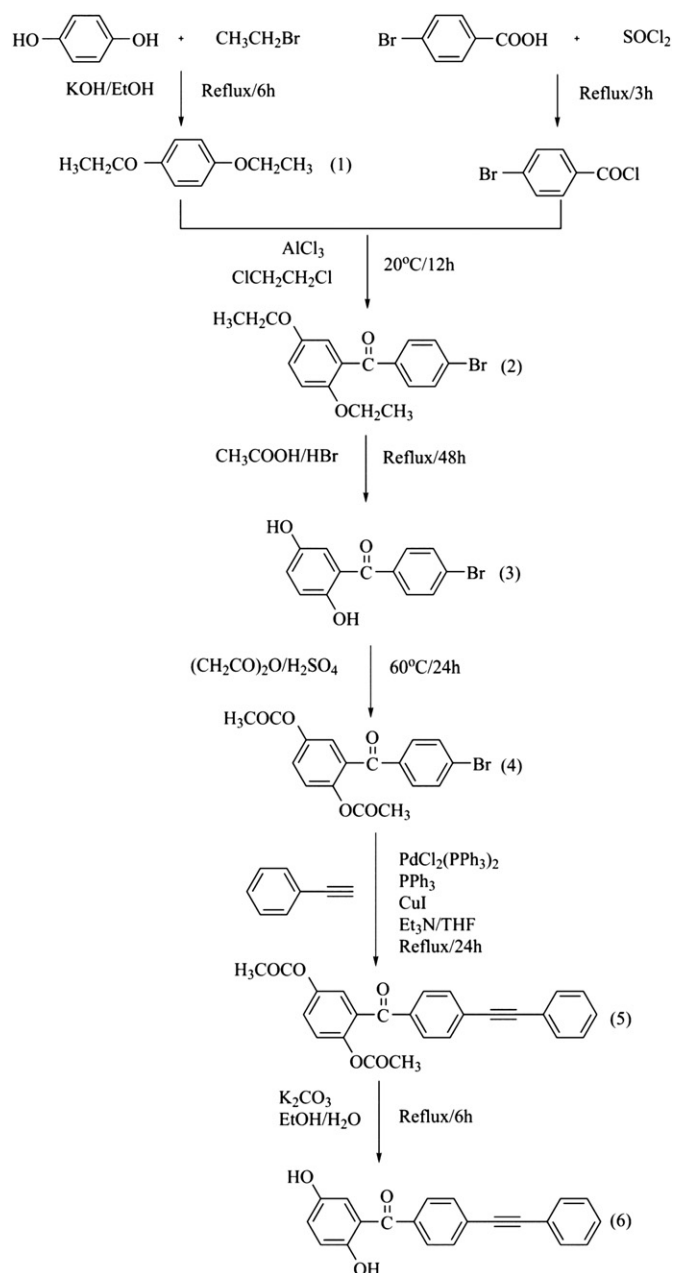


Fig. 1. Synthesis of (2,5-dihydroxyphenyl)(4-(2-phenylethynyl)phenyl)methanone (PEBP).

GPC analysis for PE-PAEKs was carried out only on the samples with higher PEBP content, i.e. on PE-PAEK50, PE-PAEK60, PE-PAEK80 and PE-PAEK100. This is due to the fact that only these samples were completely soluble in tetrahydrofuran. Therefore, only the reliable GPC results are listed in Table 1. It could be found that PE-PAEKs have number-average molecular weight between 18,000 and 12,000.

In order to confirm the composition of PE-PAEKs, elemental analysis was performed. Before analysis, the samples were Soxhlet-extracted with methanol for 48 h to ensure the complete removal of residue monomers. Finally, the samples were dried under vacuum for 48 h at 60°C . It could be found that the experimental carbon contents and hydrogen contents determined by elemental analysis were similar to the theoretical values (Table 1). Therefore, it might be believed that the composition of the obtained PE-PAEKs was in accordance with the designed ones.

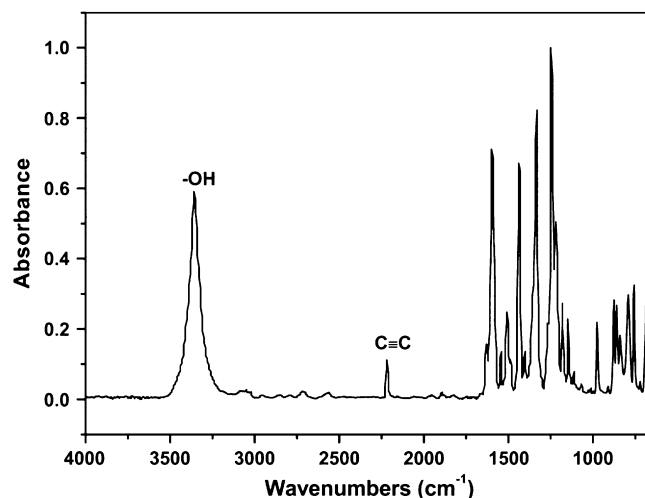


Fig. 2. FTIR spectrum of PEBP (embedded in KBr).

DSC analysis was performed to measure the glass-transition temperature of PE-PAEKs. Shown in Fig. 5 are the DSC profiles of PE-PAEKs as well as the pristine PAEK, and the values are listed in Table 1. For the pristine PAEK, the T_g was indiscernible. Only melting temperature was detected around 310°C . For the PE-PAEKs, the T_g values depended on the PEBP content. With the increase in the content of PEBP, the T_g value of PE-PAEKs increased from 160°C to 199°C , which might be due to the steric hindrance of bulky pendant phenylethynyl groups [24].

3.3. Solubility and WAXD of polymers

The solubility of the polymers was examined in various organic solvents at room temperature with a concentration of 8–10% (w/v). Shown in Table 2 is the solubility of PE-PAEKs and the pristine PAEK. Compared with the pristine PAEK, which was insoluble in ordinary organic solvents, the solubility of PE-PAEKs was improved. When the content of PEBP (relative to total bisphenols) exceeded 50 mol%, the resultant polymers exhibited excellent solubility in chlorinated solvent such as dichloromethane and chloroform, and soluble in polar aprotic solvent such as *N*-methyl-2-pyrrolidone (NMP), and also soluble in tetrahydrofuran (THF). The PE-PAEKs were insoluble in methanol and acetone.

It has been well known that PEEK derived from hydroquinone and 4,4'-difluorobenzophenone was insoluble in most known organic solvent at ambient temperature due to its semicrystalline property [1,2,7]. Bulky pendant groups and asymmetric structure could improve the solubility to some extent due to the decrease in crystallinity. That might be evidenced by WAXD.

Shown in Fig. 6 are WAXD patterns of PE-PAEKs and the pristine PAEK. The pristine PAEK showed four obvious sharp peaks. For PE-PAEK20 and PE-PAEK40, the intensity of the peaks decreased, and the diffraction peaks became wider. In the case of the polymers with higher PEBP content, their diffraction peaks were further broadened, and no real sharp peaks were observed. These indicated that with increase in PEBP content, the PE-PAEKs changed from semicrystalline to amorphous. The decrease in the crystallinity led to easier permeation of solvent; therefore, the solubility was improved.

3.4. Curing behavior of polymers

Phenylethynyl groups could undergo curing reaction upon heating and the thermal curing mechanism has been widely investigated [25–27]. However, due to the complexity of the curing

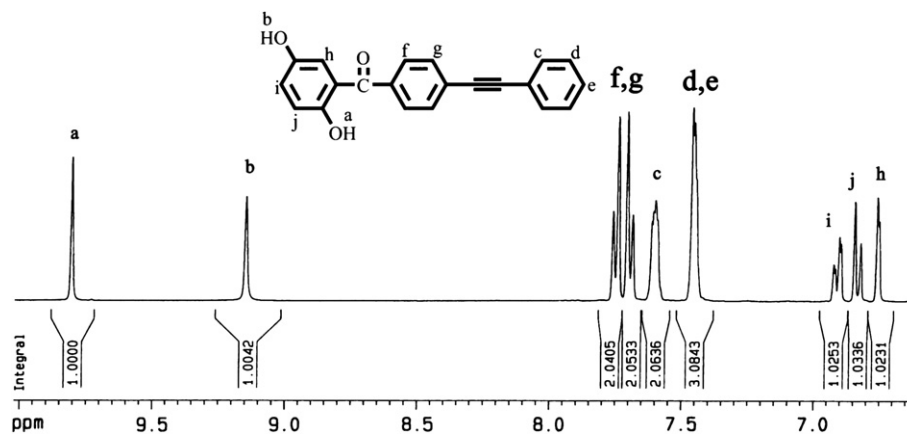


Fig. 3. ^1H NMR spectrum of PEBP (400 MHz, solvent: $\text{DMSO}-d_6$).

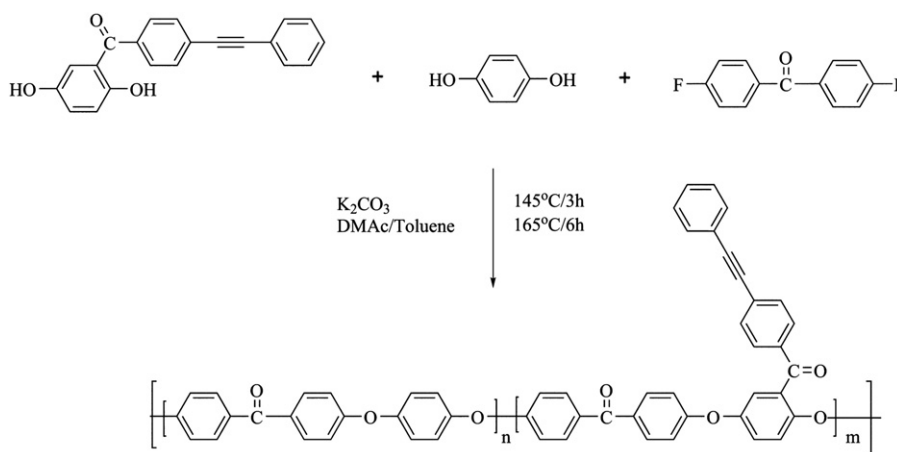


Fig. 4. Synthesis of poly(aryl ether ketone)s containing pendant phenylethynyl moieties (PE-PAEKs).

reaction and insolubility of the cured material, the curing mechanism of this system is still poorly understood. It is generally believed that the curing reaction of phenylethynyl groups was through a radical polymerization mechanism and the proposed curing reaction includes the ethynyl to ethynyl reaction to form double bonds, and a minor reaction of double bond to further form single bond [25].

FTIR spectrum could provide some helpful information on curing reaction. Therefore, FTIR spectroscopy was used as the analytical tool to monitor the change of phenylethynyl groups during curing process. Shown in Fig. 7 is the FTIR profiles of PE-PAEK80 cured at 370 °C for different times. The characteristic band corresponding to the triple bond ($\text{C}\equiv\text{C}$) of phenylethynyl groups completely disappeared upon curing for 1 h at 370 °C. It meant that

Table 1
Synthesis and characterization of poly(aryl ether ketone)s containing pendant phenylethynyl moieties

Polymers	PEBP:HQ:DF (mol%) ^a	M_n^b	M_w/M_n^b	Yield (%)	T_g^c (°C)	Elemental analysis		
						Calcd	Found	
PAEK	0:100:105	–	–	89	–	Calcd	79.16	4.20
						Found	77.97	4.20
PE-PAEK20	20:80:105	–	–	84	160	Calcd	79.91	4.18
						Found	79.30	4.37
PE-PAEK40	40:60:105	–	–	85	168	Calcd	80.66	4.16
						Found	80.03	4.35
PE-PAEK50	50:50:105	18,500	3.49	95	171	Calcd	81.04	4.15
						Found	80.80	4.50
PE-PAEK60	60:40:105	18,600	3.46	80	179	Calcd	81.41	4.13
						Found	81.01	4.45
PE-PAEK80	80:20:105	18,400	3.37	95	192	Calcd	82.16	4.11
						Found	81.51	4.22
PE-PAEK100	100:0:105	12,500	2.42	67	199	Calcd	82.91	4.09
						Found	81.78	4.43

^a Feed ratio of phenylethynyl-contained bisphenol monomer (PEBP), hydroquinone (HQ) and 4,4'-difluorobenzophenone (DF).

^b Determined by GPC.

^c Measured by DSC with a heating rate of 10 °C/min in nitrogen.

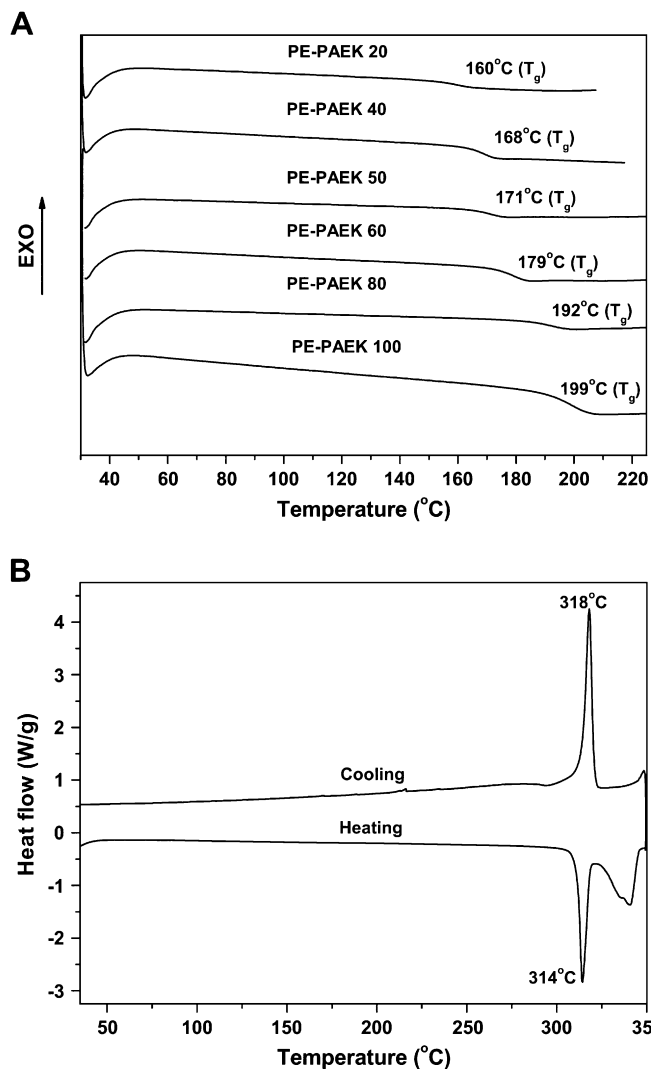


Fig. 5. DSC profiles of the uncured PE-PAEKs (A) and the pristine PAEK (B) (heating rate: 10 °C/min, in nitrogen).

phenylethynyl groups could undergo thermal curing reaction at 370 °C to form crosslinking network.

3.5. Thermal properties of polymers

The glass-transition temperature of the cured polymers was determined using dynamic mechanical analysis (DMA). The T_g was defined as the peak temperature of loss factor, $\tan \delta$.

Shown in Fig. 8 are the DMA profiles of PE-PAEKs. Compared with the commercial PEEK with a T_g of around 140 °C (determined by DMA) [28,29], it was evident that the T_g of PE-PAEKs increased considerably, which might be due to the crosslinking structure. Formation of crosslinking structure could reduce the mobility of the

Table 2
Solubility of poly(aryl ether ketone)s containing pendant phenylethynyl moieties

Polymers	THF	CH ₂ Cl ₂	CHCl ₃	NMP	MeOH	Acetone
PAEK	–	–	–	–	–	–
PE-PAEK20	–	–	–	–	–	–
PE-PAEK40	–	–	–	–	–	–
PE-PAEK50	+	+	+	+	–	–
PE-PAEK60	+	+	+	+	–	–
PE-PAEK80	+	+	+	+	–	–
PE-PAEK100	+	+	+	+	–	–

+: Soluble; -: insoluble.

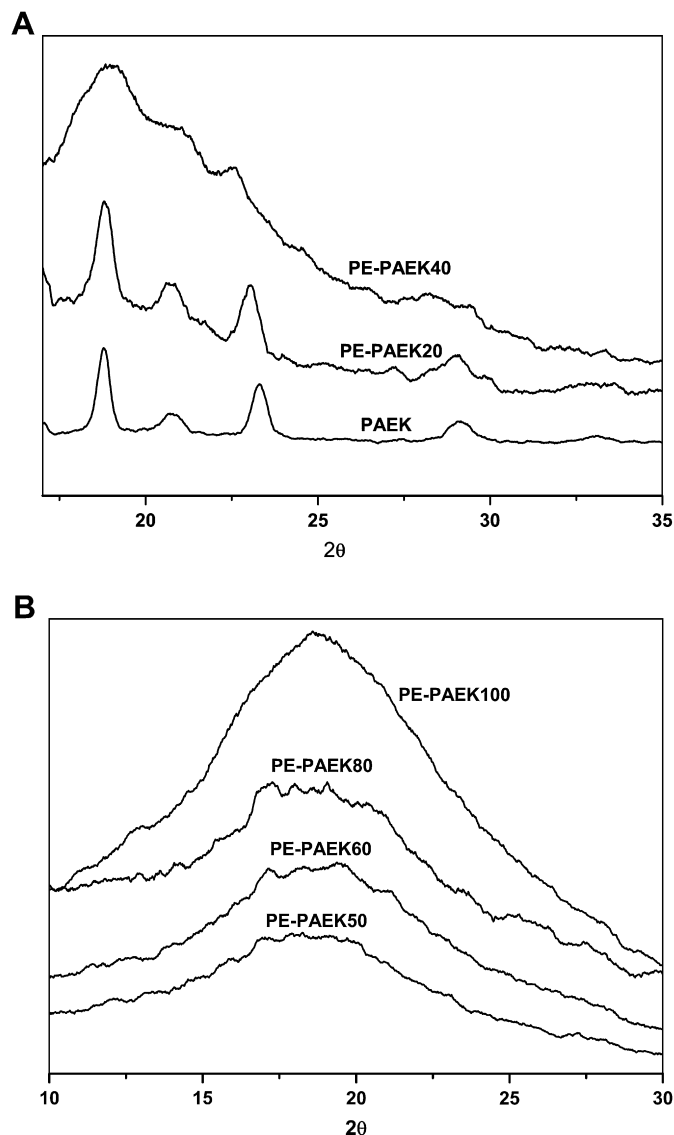


Fig. 6. WAXD patterns of the uncured PE-PAEKs and the pristine PAEK.

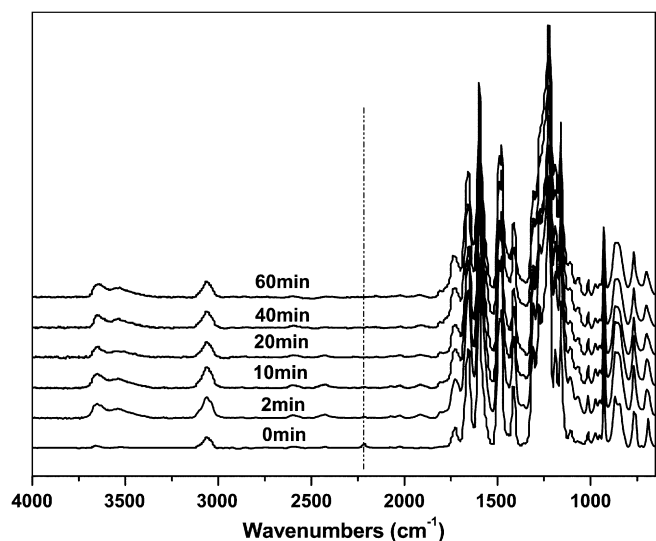


Fig. 7. FTIR spectra of PE-PAEK80 cured at 370 °C for different times in air (embedded in KBr).

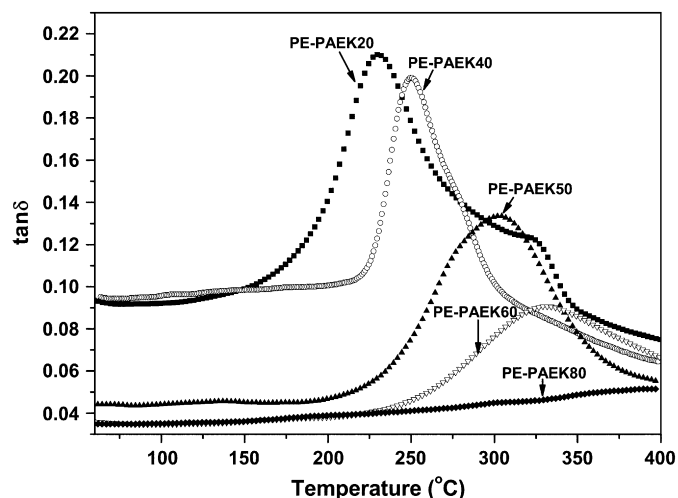


Fig. 8. DMA profiles of the cured PE-PAEKs (heating rate: 5 °C/min, frequency: 1 Hz, in nitrogen).

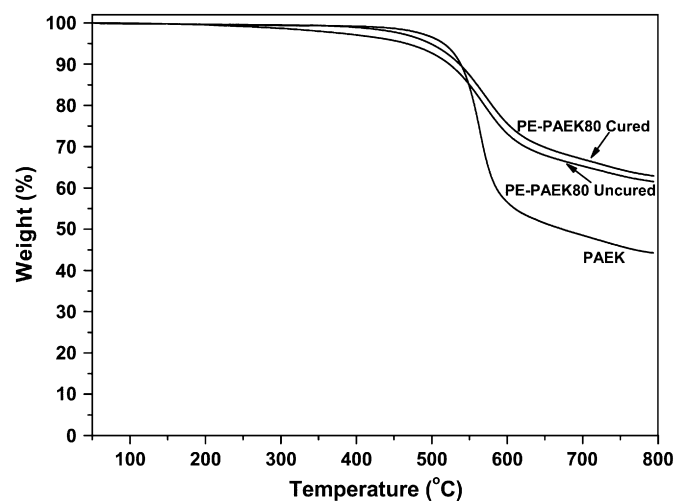


Fig. 9. TGA profiles of the uncured and cured PE-PAEK80 and pristine PAEK (heating rate: 10 °C/min, in nitrogen).

molecular chains; therefore relaxation of molecular chains became difficult. With increase in the content of PEBP in polymer, the T_g increased. For the cured PE-PAEK20, the T_g was 230 °C. For the cured PE-PAEK80, no relaxation behavior was detected in the range of experiment. This indicated that the T_g of PE-PAEK80 should be higher than 400 °C. The higher T_g might be attributed to the higher crosslinking density.

Table 3
Thermal properties of poly(aryl ether ketone)s containing pendant phenylethynyl moieties

Polymers	T_g^a (°C)	T_d^b (°C)		Yield ^c (%)	
		Uncured	Cured	Uncured	Cured
PAEK	–	514	–	38.69	–
PE-PAEK20	230	496	520	57.25	55.77
PE-PAEK40	250	474	507	57.09	60.92
PE-PAEK50	303	471	501	58.76	60.07
PE-PAEK60	331	484	503	59.78	65.46
PE-PAEK80	>400	459	500	55.89	62.73
PE-PAEK100	>400	491	507	66.59	67.37

^a Measured by DMA with a heating rate of 5 °C/min in nitrogen. Samples were cured at 370 °C for 1 h in an air oven.

^b Onset temperature for 5% weight loss measured by TGA with a heating rate of 10 °C/min in nitrogen.

^c Char yield at 800 °C measured by TGA.

The thermal stability of the uncured and cured PE-PAEKs as well as the pristine PAEK was determined using thermogravimetric analysis. The temperature at which 5 wt% loss occurs was indicative of the thermal stability. Shown in Fig. 9 are the typical thermogravimetric profiles of the uncured and cured PE-PAEK80 as well as the pristine PAEK, and the values are compiled in Table 3. Compared with the uncured PE-PAEKs, the 5 wt% loss temperatures of the cured PE-PAEKs were increased, which might result from the formation of crosslinking structure. Compared with the pristine PAEK, the thermal stability of the cured PE-PAEKs was slightly decreased. However, the 5 wt% loss temperature of PE-PAEKs was above 500 °C. Furthermore, char residue of PE-PAEKs was higher than that of the pristine PAEK. For the pristine PAEK, the char residue at 800 °C was 38%; while for the cured PE-PAEK100, the char residue was 67%. Higher char residue at high temperature might be ascribed to the high char concentration of phenylethynyl groups.

As mentioned above, the phenylethynyl-contained PAEK possessed higher T_g and good thermal stability, and might be a hopeful candidate as a matrix for high performance composite resins.

4. Conclusion

A series of novel poly(aryl ether ketone)s containing pendant phenylethynyl moieties have been prepared by a one-pot nucleophilic substitution reaction. Incorporation of bulky pendant phenylethynyl groups into molecular chains disrupted the chain packing. The resultant polymers displayed improved solubility in organic solvents. The phenylethynyl-contained poly(aryl ether ketone)s could undergo thermal curing reaction at elevated temperature. The cured polymers exhibited higher glass-transition temperature together with excellent thermal stability.

References

- [1] Matsumura S, Kihara N, Takata T. *Macromolecules* 2001;34:2848–53.
- [2] Wu C, Bo S, Siddiq M, Yang GJ, Chen TL. *Macromolecules* 1996;29:2989–93.
- [3] Meng YZ, Hlil AR, Hay AS. *J Polym Sci Part A Polym Chem* 1999;37:1781–8.
- [4] Rae PJ, Brown EN, Orler EB. *Polymer* 2007;48:598–615.
- [5] Gao Y, Jian XG, Xuan YG, Xiang S, Liang P, Guiver MD. *J Polym Sci Part A Polym Chem* 2002;40:3449–54.
- [6] Li JH, Lee YM. *Macromol Chem Phys* 2006;207:1880–7.
- [7] Ohno M, Takata T, Endo T. *Macromolecules* 1994;27:3447–8.
- [8] Liu BJ, Hu W, Chen CH, Jiang ZH, Zhang WJ, Wu ZW, et al. *Polymer* 2004;45:3241–7.
- [9] Baek JB, Tan LS. *Polymer* 2003;44:3451–9.
- [10] Taguchi Y, Uyama H, Kobayashi S. *J Polym Sci Part A Polym Chem* 1997;35:271–7.
- [11] Kimura K, Nishichi A, Yamashita Y. *Polym Adv Technol* 2004;15:313–9.
- [12] Walker KA, Markoskj LJ, Moore JS. *Macromolecules* 1993;26:3713–6.
- [13] Yue XG, Zhang HB, Chen WH, Wang YS, Zhang SL, Wang GB, et al. *Polymer* 2007;48:4715–22.
- [14] Gao CP, Hay AS. *Polymer* 1995;36:4141–6.
- [15] Chen JH, Maekawa Y, Asano M, Yoshida M. *Polymer* 2007;48:6002.
- [16] Vaughan AS, Stevens GC. *Polymer* 2001;42:8891–5.
- [17] Sasuga T, Kudoh H. *Polymer* 2000;41:185–94.
- [18] Connell JW, Smith Jr JG, Hergenrother PM. *J Macromol Sci Rev Macromol Chem Phys* 2000;C40:207–30.
- [19] Hergenrother PM. *High Perform Polym* 2003;15:3–45.
- [20] Ma XY, Lv ZH, Wang D, Guan SW, Chen CH, Wang GB, et al. *J Photochem Photobiol A Chem* 2007;188:43–50.
- [21] Lee HJ, Lee EM, Lee MH, Oh MC, Ahn JH, Han SG, et al. *J Polym Sci Part A Polym Chem* 1998;36:2881–7.
- [22] Ma XY, Liu BJ, Wang D, Wang GB, Guan SW, Jiang ZH. *Mater Lett* 2006;60:1369–73.
- [23] Kimura K, Nishichi A, Yamashita Y. *Polym J* 2002;34:209–18.
- [24] Huang WY, Liaw BR, Chang MY, Han YK, Huang PT. *Macromolecules* 2007;40:8649–57.
- [25] Fang XM, Xie XQ, Simone CD, Stevens MP, Scola DA. *Macromolecules* 2000;33:1671–81.
- [26] Fang XM, Rogers DF, Scola DA, Stevens MP. *J Polym Sci Part A Polym Chem* 1998;36:461–70.
- [27] Roberts CC, Apple TM, Wnek GE. *J Polym Sci Part A Polym Chem* 2000;38:3486–97.
- [28] Goodwin AA, Hay JN. *J Polym Sci Part B Polym Phys* 1998;36:851–9.
- [29] David L, Etienne S. *Macromolecules* 1992;25:4302–8.