

Synthesis and Characterization of Novel Soluble Cardo Poly(arylene ether ketone)s Containing Xanthene Structures

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ABSTRACT: 9,9-Bis(4-hydroxyphenyl)xanthene (BHPX), a bisphenol monomer, was synthesized in 82% yield from xanthenone in a one-pot, two-step synthetic procedure. Four novel aromatic poly(ether ketone)s (PEKs) based on BHPX were prepared via a nucleophilic aromatic substitution polycondensation with four difluorinated aromatic ketones. The polycondensation proceeded in tetramethylene sulfone in the presence of anhydrous potassium carbonate and afforded the new cardo PEKs in nearly quantitative yields with inherent viscosities of 0.77–0.85 dL/g. High molecular weight PEKs having number-average molecular weights (M_n 's) in the range of 38,900–40,600 g/mol with the polydispersity index ranged from 1.97 to 2.06 are all amorphous and show high glass transition

temperatures ranging from 210°C to 254°C, excellent thermal stability, and the temperatures at the 5% weight loss are over 538°C with char yields above 60% at 700°C in nitrogen. These new PEKs are all soluble in polar aprotic solvents such as *N*-methyl-2-pyrrolidone and *N,N*-dimethylacetamide and could also be dissolved in chloroform and tetrahydrofuran. All the polymers formed transparent, strong, and flexible films with tensile strengths of 78–84 MPa, Young's moduli of 2.54–3.10 GPa, and elongations at break of 14–18 %. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 570–576, 2009

Key words: Cardo poly(aryl ether ketone)s; pendant xanthene group; soluble

INTRODUCTION

Aromatic poly(ether ketone)s (PEKs), including poly(ether ether ketone) (PEEK), poly(ether ketone ketone) (PEKK), and poly(ether ether ketone ketone) (PEEKK) are a class of high performance engineering thermoplastics known for their excellent combination of chemical, physical, and mechanical properties. This class of advanced materials is currently receiving considerable attention for potential applications in aerospace, automobile, electronics, and other high technology fields.^{1–4} However, because of their aromatic structure and semicrystallinity, PEKs generally are insoluble in common organic solvents. Their insolubility and high melting temperatures make these polymers difficult to process and fabricate. Therefore, many efforts have been directed toward

synthesizing soluble PEKs without scarification of their desired properties. Several approaches have been investigated to improve their solubility such as the alteration the order and ratio of ether–ketone linkage⁵ as well as the ratio of meta and para phenyl substitution,⁶ the insertion of $-\text{CR}_2$ ^{7,8} and sulfone groups,^{9–11} the introduction of pendant groups,^{12–17} and the incorporation of a noncoplanar structure^{18–20} in the backbone of the polymeric chain. The introduction of pendant loops along the polymer backbone has been shown to impart greater solubility, enhanced rigidity, as well as better mechanical and thermal properties. It has been demonstrated that the incorporation of cardo groups such as phthalein and fluorine^{8,21–25} groups into the backbone of PEKs results in polymers with enhanced solubility, processability, and good thermal stability. To the best of our knowledge, although poly(aryl ether)s^{26,27} and poly(aryl ester)s²⁸ containing xanthene cardo groups in the polymeric chain were previously documented, PEKs containing xanthene cardo groups within the polymeric chain have not been reported. Based on the above studies reported thus far, we have here designed and synthesized several novel cardo PEKs by reaction of a bisphenol monomer, 9,9-bis(4-hydroxyphenyl)xanthene (BHPX) with various difluorinated aromatic ketones in tetramethylene

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sulfone and in the presence of potassium carbonate as an acid acceptor. The solubility, crystallinity, thermal stability, and mechanical property of these new cardo PEKs with 9,9-xanthene moiety in the main chain are investigated.

EXPERIMENTAL

Materials

Xanthenone (Jiangsu Huatai Reagent Co., China), phenol (Shanghai Chemical Reagent Co., China), thionyl chloride (Shanghai Chemical Reagent Co., China) was used as received. Commercially available xylene was refluxed with sodium and distilled under reduced pressure and stored over 4 Å molecular sieve prior to use. Anhydrous K_2CO_3 (Beijing Chemical Reagent Co., China) was dried in vacuum at 100°C before use. Tetramethylene sulfone (TMS) (Aldrich) was dried with 4 Å molecular sieve and distilled over NaOH pellets under reduced pressure. The middle fractions were collected and stored over molecular sieves. 4,4'-Difluorobenzophenone (mp = 103–104°C) (**4a**), 1,4-bis(4-fluorobenzoyl)benzene (mp = 219–220°C) (**4b**), 4,4'-bis(4-fluorobenzoyl)biphenyl (mp = 269–270°C) (**4c**), and 4,4'-bis(4-fluorobenzoyl)diphenyl ether (**4d**) (mp = 214–216°C) were prepared in our lab according to the standard procedures. The other reagents and solvents such as *N*-methyl-2-pyrrolidone (NMP), *N,N'*-dimethylformamide (DMF), *N,N'*-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), chloroform, toluene, methanol, acetone, tetrahydrofuran, and concentrated sulfuric acid were obtained from commercial sources and used as received.

Monomer synthesis

Preparation of 9,9-Bis(4-hydroxyphenyl)xanthene

In a 250-mL round-bottom flask, xanthenone (**1**) (19.6 g, 0.1 mol) was refluxed in thionyl chloride (150 mL) for 5 h and stood 18 h to convert it to the 9,9-dichloroxanthene (**2**) according to literature method.²⁹ The excess of thionyl chloride was removed under vacuum, the dichloride (**2**) was washed with petroleum ether, dried under vacuum, and then dissolved in xylene and phenol (23.5 g, 0.25 mol) was added. The mixture was refluxed for 8 h and the xylene and excess of phenol were removed under vacuum and the crude product was recrystallized from toluene to afford 30 g (82% yield) of purplish-red acicular crystals, m.p. 239–240°C (lit.²⁸ 241°C). ¹H-NMR ($CDCl_3$): δ = 7.26 (t, *J* = 8.0 Hz, 2 H), 7.14 (d, *J* = 8.0 Hz, 2 H), 7.04 (t, *J* = 8.0 Hz, 2 H), 6.93 (d, *J* = 8.0 Hz, 2 H), 6.83 (d, *J* = 8.8 Hz, 4 H), 6.70 (d, *J* = 8.8 Hz, 4 H), 4.68 (br s, 2 H); ¹³C-NMR ($CDCl_3$): δ = 155.96, 151.92, 136.64, 130.93,

130.90, 130.25, 128.41, 123.57, 116.48, 115.01, 52.74; Elem. Anal. Calcd for $C_{25}H_{18}O_3$ (366.42 g/mol): C, 81.95 %; H, 4.95%. Found: C, 81.90 %; H, 4.87 %; FTIR (KBr): ν_{max} = 3065, 3033, 1611, 1595, 1508, 1444, 1238, 1175, 870, 759 cm^{-1} .

Polymer synthesis

Poly(ether ether ketone) (5a)

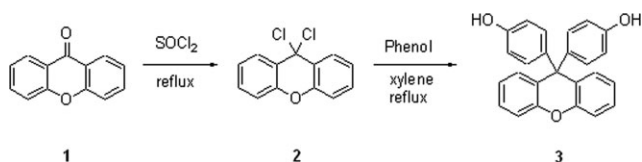
Preparation of PEK was carried out using similar procedure described.¹³ In a typical experiment, PEEK (**5a**), which derived from BHPX (**3**) and 4,4'-difluorobenzophenone (**4a**), was prepared as follows: To a 150-mL three-necked flask equipped with a mechanical stirrer, a nitrogen inlet with a thermometer, and a Dean-Stark trap with a condenser, were added **3** (9.1604 g, 0.025 mol), **4a** (5.4551 g, 0.025 mol), anhydrous K_2CO_3 (4.485 g, 0.0325 mol), TMS (45 mL) and toluene (32 mL). The system was allowed to reflux for 2 h, and then the toluene was removed by distillation, and reaction mixture was heated to 210°C and stirred at this temperature under nitrogen for 2 h. After cooling, the viscous solution was poured into methanol-water solution (500 mL), and the precipitated polymer was collected by filtration and then pulverized into a powder using a blender. The polymer powder was washed thoroughly several times with hot water, and then dissolved with chloroform, and precipitated in methanol twice. After filtration, the white polymer (**5a**) was dried at 120°C under vacuum overnight with a yield of 97%. ¹H-NMR ($CDCl_3$): δ = 7.78 (d, *J* = 8.4 Hz, 4 H), 7.31–7.26 (m, 2 H), 7.19 (d, *J* = 8.0 Hz, 2 H), 7.09–6.94 (m, 16 H); ¹³C-NMR ($CDCl_3$): δ = 194.15, 160.92, 154.36, 152.46, 141.73, 132.47, 132.21, 131.57, 129.99, 129.92, 128.17, 123.07, 119.12, 117.54, 116.66, 53.51; FTIR (KBr): ν_{max} = 1649 (C=O), 1230 (Ar—O—Ar).

Poly(ether ether ketone) (5b)

PEEK (**5b**) was synthesized by the polymerization of BHPX (**3**) with 1,4-bis(4-fluorobenzoyl)benzene (**4b**). The procedure is similar to the synthesis of **5a**. ¹H-NMR ($CDCl_3$): δ = 7.84–7.82 (m, 8 H), 7.32–7.26 (m, 2 H), 7.20 (d, *J* = 8.0 Hz, 2 H), 7.11–6.97 (m, 16 H); FTIR (KBr): ν_{max} = 1660 (C=O), 1228 (Ar—O—Ar).

Poly(ether ether ketone diphenyl ketone) (5c)

Poly(ether ether ketone diphenyl ketone) (PEEKDK) (**5c**) was prepared from BHPX (**3**) and 4,4'-bis(4-fluorobenzoyl)biphenyl (**4c**), according to the same procedure used for **5a**. ¹H-NMR ($CDCl_3$): δ = 7.89–7.84 (m, 8 H), 7.74 (d, *J* = 8.0 Hz, 4 H), 7.32–7.26 (m, 2



Scheme 1 Preparation of 9,9-bis(4-hydroxyphenyl)xanthone (BHPX).

H), 7.20 (d, $J = 8.0$ Hz, 2 H), 7.11–6.96 (m, 16 H); FTIR (KBr): $\nu_{\max} = 1660$ (C=O), 1225 (Ar–O–Ar).

Poly(ether ether ketone ether ketone) (5d)

Poly(ether ether ketone ether ketone) (PEEKEK) (5d) was synthesized from BHPX (3) and 4,4'-bis(4-fluorobenzoyl)diphenyl ether (4d) using the procedure similar to the preparation of 5a. $^1\text{H-NMR}$ (CDCl_3): $\delta = 7.84$ – 7.79 (m, 8 H), 7.31– 7.26 (m, 2 H), 7.20 (d, $J = 8.0$ Hz, 2 H), 7.13– 6.96 (m, 20 H); FTIR (KBr): $\nu_{\max} = 1657$ (C=O), 1228 (Ar–O–Ar).

Measurements

The ^1H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on Bruker Avance 400 MHz spectrometer using dimethyl sulfoxide- d_6 ($\text{DMSO-}d_6$) or chloroform (CDCl_3) as the solvent and with tetramethylsilane as internal standard. The FTIR spectra of the monomer and polymers in KBr pellets were determined on a Perkin-Elmer SP One FTIR spectrophotometer. Microanalyses were performed with a Carlo Erba 1106 Elemental Analyzer. Melting points were determined on X₄ melting point apparatus and are uncorrected. The glass-transition temperatures

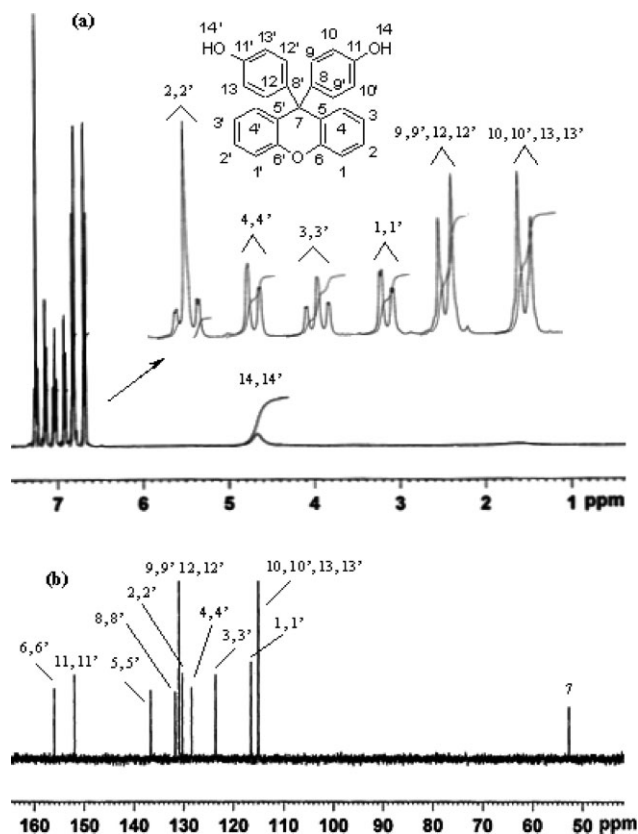
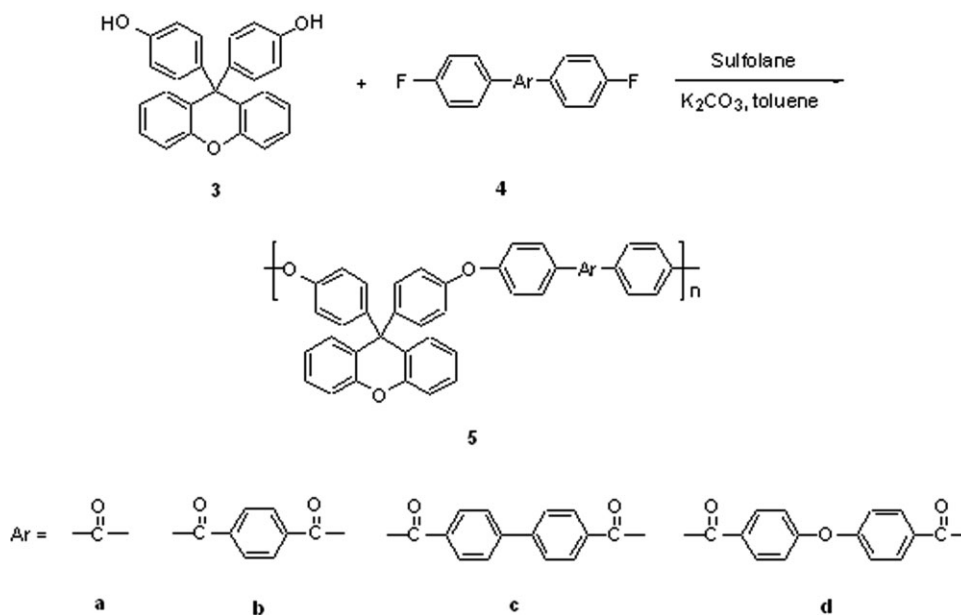


Figure 1 $^1\text{H-NMR}$ (a) and $^{13}\text{C-NMR}$ (b) spectra of BHPX.

(T_g 's) were performed on a Perkin-Elmer DSC-7 instrument at a heating rate of $20^\circ\text{C}/\text{min}$ under nitrogen protection. The second scan was immediately initiated after the sample was cooled to room temperature. The T_g values were reported from the second scan after the first heating and quenching,



Scheme 2 Synthesis of novel aromatic PEKs (5a–5d).

TABLE I
Physical Properties of PEKs (5a–5d)

| PEK | Yield (%) | η_{inh} (dL/g) ^a | M_w (g/mol) ^b | M_n (g/mol) ^b | M_w/M_n |
|-----|-----------|----------------------------------|----------------------------|----------------------------|-----------|
| 5a | 97 | 0.82 | 79,900 | 40,500 | 1.97 |
| 5b | 96 | 0.77 | 80,400 | 40,600 | 1.98 |
| 5c | 98 | 0.85 | 81,100 | 39,600 | 2.04 |
| 5d | 97 | 0.80 | 80,200 | 38,900 | 2.06 |

^a Measured at a polymer concentration of 0.5 g/dL in H₂SO₄ at 25 ± 0.1°C.

^b Molecular weight was determined by GPC in chloroform with polystyrene as standard.

and taken from the midpoint of the change in the slope of the baseline. The thermal stability of the polymers from 50 to 800°C was determined with a Seiko SSC-5200 thermogravimetric analysis (TGA) at a heating rate of 10°C/min under a protective nitrogen atmosphere (120 mL/min). The inherent viscosity ($\eta_{inh} = \ln \eta_r/c$) was obtained using conc. H₂SO₄ solutions with a concentration of 0.50 g/dL in an

Ubbelohde viscometer at 25 ± 0.1°C. Molecular weights were determined by a gel permeation chromatography (GPC) with polystyrene calibration using a Waters 510 HPLC equipped with 5- μ m phenogel columns (linear, 3 × 500 Å) arranged in series and a UV detector at 254 nm using tetrahydrofuran as eluent. Polymer samples were dissolved in CHCl₃, filtered, precipitated in methanol and dried under vacuum at room temperature before performing GPC measurements. The solubility of the polymers was determined with 2 mg of a polymer in 3 mL of a solvent. The wide-angle x-ray diffraction measurements were conducted on at room temperature (ca. 25°C) on power with a Rigaku Geiger Flex D-Max III x-ray diffractometer, using Ni-filtered CuK α radiation (operating at 40 kV and 15 mA); the scanning rate was 2°/min over a range of 2 θ = 2–40°. Mechanical properties of the thin films (about 0.2 mm, cast from NMP solutions onto the glass plates, and followed by heating at 100–150°C *in vacuo*) were evaluated at room temperature on an Instron 1121 instrument at a strain rate of 10 mm/min.

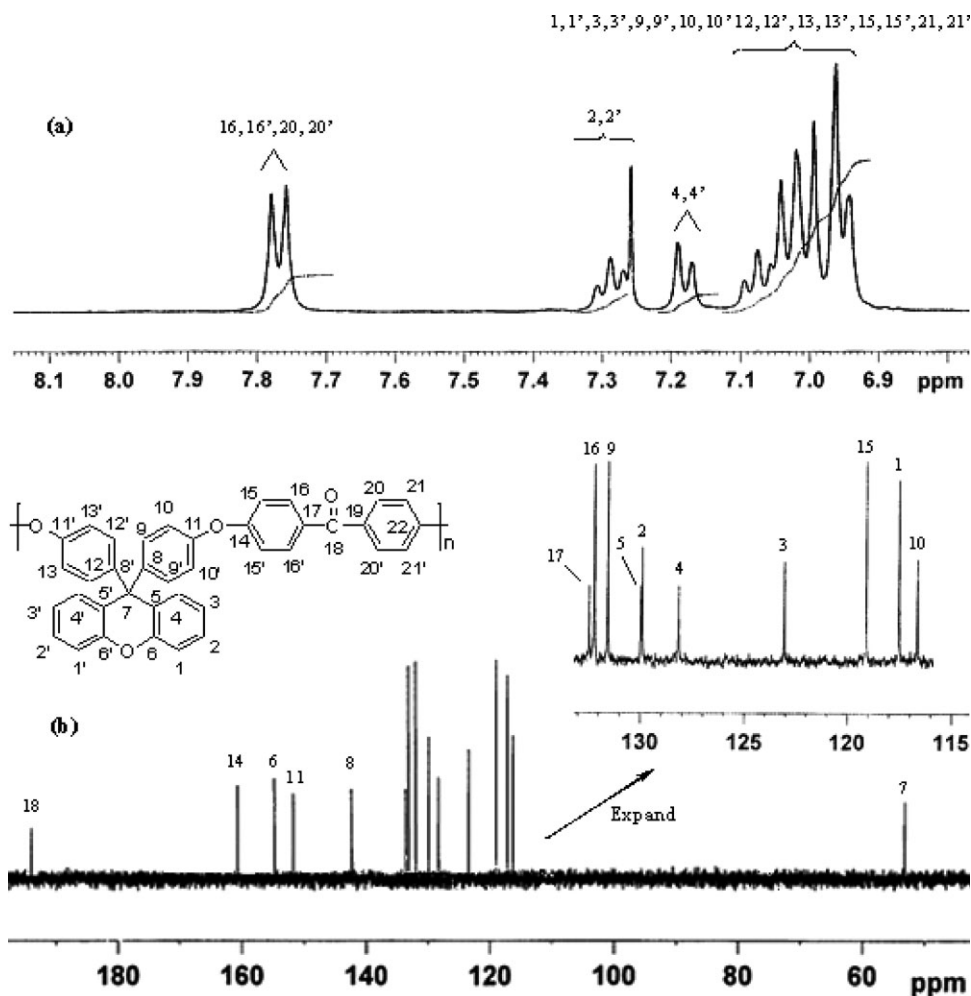


Figure 2 ¹H-NMR (a) and ¹³C-NMR (b) spectra of PEEK (5a).

RESULTS AND DISCUSSION

Synthesis of BHPX

Scheme 1 outlines the synthetic route applied for the synthesis of the bisphenol monomer, 9,9-bis(4-hydroxyphenyl)xanthene (BHPX). In general, bisphenols could be prepared by the condensation of ketone compounds with excess phenol catalyzed by acid such as hydrogen chloride and 3-mercaptopropionic acid. However, the reaction of xanthenone and phenol under the similar conditions did not afford the desired BHPX. It might be resulted from the steric hindrance of the phenyl groups of the xanthenone. Previously, BHPX was synthesized from 9,9-dichloroxanthene with excess of phenol in the presence of 3-mercaptopropionic acid,²⁸ but the yield of BHPX was low (14%). After a series of experiments, 82% yield of BHPX was obtained by reaction of xanthone with thionyl chloride, affording 9,9-dichloroxanthene (**2**), followed by treatment with phenol in refluxing xylene in a one-pot, two-step synthetic procedure.

The structure of BHPX was confirmed by elemental analysis, FTIR, ¹H-, and ¹³C-NMR spectroscopic techniques. In the FTIR spectrum, BHPX shows a characteristic band of hydroxy group in the region of 2500 to 3000 cm⁻¹ and a strong absorption of aryl ether group at 1238 cm⁻¹. The ¹H- and ¹³C-NMR spectra of BHPX are given in Figure 1. Assignments of each carbon and proton are also given in the figure, and these spectra agree with the proposed molecular structure.

Polymer synthesis

Polymerization of BHPX with four different difluorinated aromatic ketones was carried out in the presence of K₂CO₃ in TMS as the solvent at 210°C after removing the water from the reaction system by the azeotropic distillation of toluene, as shown in

TABLE II
Thermal Properties of PEKs (5a–5d)

| PEK | <i>T_g</i> (°C) ^a | <i>T_{d5}</i> (°C) ^b | <i>T_{d5}</i> (°C) ^c | <i>T_{d10}</i> (°C) ^d | <i>R_w</i> (%) ^e |
|-----|--|---|---|--|---------------------------------------|
| 5a | 210 | 558 | 553 | 570 | 66 |
| 5b | 229 | 562 | 553 | 572 | 66 |
| 5c | 254 | 556 | 552 | 572 | 67 |
| 5d | 236 | 538 | 525 | 558 | 64 |

^a From the second heating trace of DSC measurements conducted at a heating rate of 20°C/min.

^b 5% weight loss temperatures measured by TGA at a heating rate of 10°C/min under nitrogen.

^c 5% weight loss temperatures measured by TGA at a heating rate of 10°C/min in air.

^d 10% weight loss temperatures measured by TGA at a heating rate of 20°C/min under nitrogen.

^e Residual weight percentages at 700°C under nitrogen.

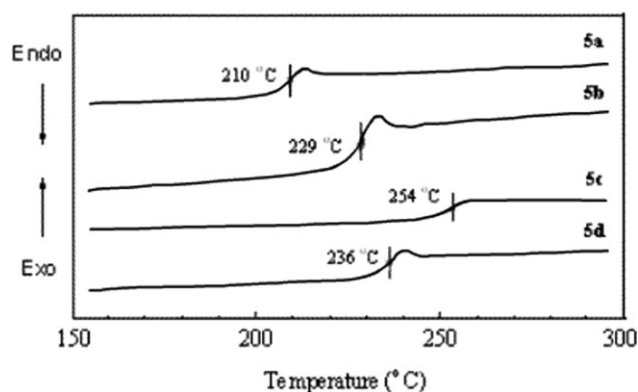


Figure 3 DSC curves of the PEKs (5a–5d).

Scheme 2. Inherent viscosities (η_{inh}) ranging from 0.77 to 0.85 dL/g reveal that high molecular weight polymers were readily obtained in a shorter reaction time (2 h) in TMS medium for ether ketone type polymers. Additionally, solvents such as NMP, DMAc, and DMSO in place of TMS were also tried, the similar results can be obtained, but the longer reaction time (3–4 h) was required to drive the reaction. As seen from Table I, the number-average molecular weights (M_n 's) were in the range of 38,900–40,600 g/mol, and the polydispersities values of these polymers ranged from 1.97 to 2.06, as determined by gel permeation chromatography (GPC) measurements in tetrahydrofuran with polystyrene as a standard.

The chain structural features of these PEKs (5a–5d) were confirmed by FTIR and NMR spectra. The FTIR spectra of all polymers exhibited characteristic absorption bands at 1649–1660 cm⁻¹ corresponding to aryl carbonyl groups, around 1228 cm⁻¹ due to aryl ether linkages. In the ¹H-NMR spectra of these polymers, the signals at 7.88–6.94 ppm are assigned to the aromatic protons in the polymer chains. Figure 2 shows a typical set of NMR spectra for

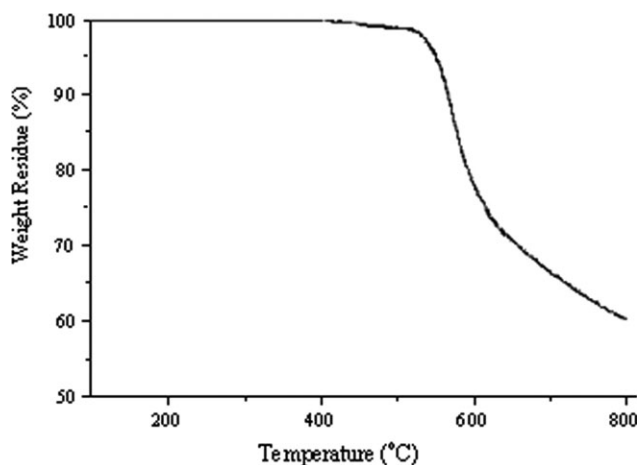


Figure 4 TGA curve of PEK (5a) in nitrogen.

TABLE III
Solubility of PEKs (5a–5d)

| PEK | DMF | DMAc | NMP | THF | DMSO | CHCl ₃ | Acetone | CH ₃ OH | Conc. H ₂ SO ₄ |
|------|-----|------|-----|-----|------|-------------------|---------|--------------------|--------------------------------------|
| 5a | ++ | ++ | ++ | ++ | -- | ++ | -- | -- | ++ |
| 5b | ++ | ++ | ++ | ++ | -- | ++ | -- | -- | ++ |
| 5c | ++ | ++ | ++ | ++ | -- | ++ | -- | -- | ++ |
| 5d | +- | ++ | ++ | ++ | -- | ++ | -- | -- | ++ |
| PEEK | -- | -- | -- | -- | -- | -- | -- | -- | ++ |
| PEKK | -- | -- | -- | -- | -- | -- | -- | -- | ++ |

+ +: soluble; --: insoluble; + -: partially soluble.

PEEK (5a). As can be seen, the spectra are in good agreement with the proposed polymer structure.

The crystallinity of these PEKs was measured by wide angle X-ray diffraction (WAXD) scans. The diffraction patterns indicated all the polymers were completely amorphous. This is reasonable because the existence of the bulky xanthene pendant group hindered chain packing and reduced intramolecular interactions. Furthermore, the amorphous nature of these polymers was reflected in their good solubility.

Thermal properties

The thermal behavior data of these new PEKs were evaluated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), as summarized in Table II. DSC curves of these polymers with no melting peak (T_m), and only a single glass transition temperature (T_g) on each curve are shown in Figure 3, which indicated that all samples were amorphous. The T_g of the PEKs obtained from the second heating trace was in the range of 210–254°C, following the increasing order of PEKK (5a), PEEKK (5b), PEEKEK (5d), PEEKDK (5c). This is explained by the introduction of carbonyl and biphenyl groups that lead to an increase in the rigidity of the polymer chains, which would increase the T_g 's of the polymers. As depicted in Table II, PEEKDK (5c) with a rigid biphenylene unit showed the highest T_g value. Compared with the conventional aromatic PEEK ($T_g = 143^\circ\text{C}$) and PEKK ($T_g = 156^\circ\text{C}$), all the PEKs displayed higher glass transition temperatures, which might mainly result from the xanthene pendant group of monomer inhibiting the polymer backbone's free rotation.

These new PEKs exhibit excellent thermal stability according to dynamic TGA results both in nitrogen and air (Table II). The representative TG diagram of PEKK (5a) in nitrogen is shown in Figure 4. Thermal stability as indicated by the temperature at which 5% weight loss (T_{d5}) and 10% weight loss (T_{d10}) were above 538°C and 558°C in nitrogen, respectively. Moreover, all the PEKs exhibited moderately char yields above 60% at 700°C in nitrogen, which

were comparable to those of conventional PEKs.³⁰ The resistance of the polymers to oxidation is suggested from their TGA behavior in air where the 5% weight loss temperature varies from 525°C to 553°C. Compared with the similar structure PEK containing-fluorine moieties ($T_{d5} = 512^\circ\text{C}$ in air),^{8,31,32} the new prepared PEKK (5a) ($T_{d5} = 553^\circ\text{C}$ in air) seemed to exhibit better thermal stability, which is due to the incorporation of the more rigid xanthene moieties to the main chain.

Solubilities and mechanical properties

The solubility behavior of the polymers in some solvents is listed in Table III. All the PEKs were found to be soluble in concentrated sulfuric acid like PEEK and PEKK. It is well known that the conventional PEEK and PEKK could not be dissolved in most known organic solvents. In sharp contrast, these new PEKs were soluble at room temperature in polar aprotic solvents NMP, DMAc and DMF (except for 5d) as well as in the less polar solvents such as chloroform and THF. The good solubility of these polymers could be attributed to the introduction of xanthene moiety, which disturb the close packing of the polymer chains and lead to the increased free volume. Therefore, it will become easy for solvents to solubilize the polymer, which is necessary in industrial processing for the polymer.

The mechanical properties of the polymer thin film cast from chloroform are summarized in Table IV. All the films were transparent, strong, and flexible. The polymer films had tensile strengths of 78–84 MPa, Young's moduli of 2.54–3.10 GPa, and

TABLE IV
Mechanical Properties of PEKs (5a–5d)

| PEK | Tensile strength (MPa) | Young's modulus (GPa) | Elongation at break (%) |
|-----|------------------------|-----------------------|-------------------------|
| 5a | 80 | 2.54 | 18 |
| 5b | 78 | 2.72 | 15 |
| 5c | 84 | 3.10 | 14 |
| 5d | 79 | 2.65 | 17 |

elongations at break of 14–18%, indicating that they are strong materials.

CONCLUSIONS

9,9-Bis(4-hydroxyphenyl)xanthene (BHPX) as a bisphenol monomer has been successfully synthesized in good yield with a one-pot, two-step procedure using xanthenone as original material. Four novel cardo aromatic PEKs were prepared from BHPX via the nucleophilic aromatic substitution polycondensation with four fluoro compounds. The resulting cardo PEKs are amorphous and have high molecular weight, high glass transition temperatures, good thermal stability and mechanical properties. These polymers have remarkably improved solubilities in common organic solvents over the conventional PEEK and PEKK. These polymers were well soluble in CHCl_3 , THF and polar solvents such as DMAc and NMP, and afforded transparent, flexible and amorphous films by solution-casting. The excellent solubility makes the polymers potential candidates for practical applications in casting processes.

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