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ORIGINAL PAPER

Synthesis and characterization of poly(aryl ether ketone)s with fluorinated phenyl in the side chain

Juan Xie · Wei-ya Peng · Guang Li · Jian-ming Jiang

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Abstract New bisphenol monomers, (4-fluorophenyl)hydroquinone (**3b**) and (3,4-difluoro phenyl)hydroquinone (**3c**), were synthesized in a two-step synthesis. Poly(aryl ether ketone)s (PAEKs) (**4a**–**c**) were derived from these fluorinated bisphenols and nonfluorinated bisphenol—phenylhydroquinone (**3a**) with 4,4′-diflourobenzophenone via a nucleophilic aromatic substitution polycondensation. The obtained polymers had inherent viscosities of 0.50–0.92 dL/g. Thermal analysis showed that the obtained PAEKs had excellent thermal properties, the glass transition temperatures ranged from 148 to 160 °C, and the temperatures at 5% weight loss (Td_5) were above 527 °C and the temperatures at 10% weight loss (Td_{10}) were above 544 °C in nitrogen. All the polymers showed excellent solubility and could dissolve in common organic solvents, such as DMSO, NMP, DMF, etc. So the films of them were easily cast from their solutions, which possessed good mechanical properties, with tensile strengths of 95.2–104.0 MPa, Young's moduli of 2.68–3.06 GPa, and elongation at break of 15–32%. Furthermore, the prepared PAEKs displayed low dielectric constants (2.75–2.95 at 1 MHz) and hydrophobic character (contact angles for water: 83.9°–98.4°).

Keywords Poly(aryl ether ketone) · Fluorinated synthesis · Solubility · Dielectric constant

Introduction

Poly(aryl ether ketone)s (PAEKs) are currently receiving considerable commercial interest as high performance engineering thermoplastics. Excellent combination of

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J. Xie · W. Peng · G. Li (✉) · J. Jiang
State Key Laboratory for Modification of Chemical Fibers and Polymer Materials,
College of Material Science and Engineering, Donghua University, Shanghai 201620, China
e-mail: lig@dhu.edu.cn

chemical, physical, and mechanical properties make them a class of important advanced materials used in aerospace, automobile, electronics, and other high technology fields [1–3]. However, conventional PAEKs show high crystallinity, resulting in their very high melting temperature and poor solubility toward common organic solvents, which makes processing difficult and thus restricts their application. Therefore, a lot of efforts have been made to improve the solubility, processability and other desired properties through structure modification, such as: varying the para\meta connectivity [4], changing the ether-to-ketone ration [5]. Groups with sp^3-hybridized atoms, such as $–CR_2–$ and $–SO_2–$ have also been introduced in the backbone of PAEKs [6]. Introduction of pedant groups onto the PAEK main chain is another important structural change [7–16].

Moreover, the increasing attention has been devoted to the preparation of fluorine-contained polymers due to their unique properties and high temperature performance. Many polymers containing fluorine have been synthesized successfully, such as fluorinated poly(triazine)s [17], fluorinated polyimides [18–23], etc. It also has been proved that the introduction of fluorine atoms or groups containing fluorine atoms into PAEK backbones could result in an improved solubility and a low dielectric constant [24–27], which was attributed to the low polarizability of the C–F bond and the increase in the free volume [28].

As part of efforts to develop highly soluble PAEKs with low dielectric constants and other desired properties, this article mainly reported two new fluorinated bisphenol monomers and their use for the preparation of novel fluorinated PAEKs. The solubility, dielectric constants, surface behavior, thermal and mechanical properties of the obtained PAEKs were also investigated and discussed.

Experiment

Materials

4-Fluoroaniline,3,4-difluoroaniline, phenylhydroquinone, and 4,4′-difluorobenzophenone were purchased from Alfa and used without purification. Commercially available 1,4-benzoquinone, zinc powder, sodium nitrite, sodium bicarbonate, and potassium carbonate were dried under vacuum prior to use. Commercially obtained *N*,*N*-dimethylacetamide (DMAc), *N*-methyl-2-pyrrolidone (NMP) and *N*,*N*-dimethylformamide (DMF) were purified by distillation under reduced pressure. All other chemicals and solvents were reagent grade and used without further purification unless otherwise noted.

Measurements

FTIR spectra were recorded on a Nicolet Magna 470 spectrometer. ^1H (400 MHz), and ^{19}F (376.5 MHz) NMR spectra were recorded on a Bruker AV 400 MHz instrument with tetramethylsilane (^1H) or $CFCl_3$ (^{19}F NMR) as a reference. Differential scanning calorimetry (DSC) analysis was performed on a TA 2900 M DSC instrument at a heating rate of 20 °C/min in nitrogen atmosphere. Glass transition temperatures (T_g) were read at the middle of the transition in the heat capacity from the second heating scan. Thermogravimetric analysis (TGA) of the samples were measured on a DuPont 2000 SDT-2960 instrument at a heating rate of 20 °C/min in nitrogen atmosphere, and Td_5 and Td_{10} were reported as the temperatures where 5 and 10% weight loss were observed, respectively. Elemental analysis was carried out on a Vario EL III elemental analyzer. Mass spectra were obtained on a Shimadzu QP-2010 mass spectrometer. Inherent viscosities ($\eta_{inh} = \ln \eta_r/c$) were measured at a concentration of 0.5 g/dL in DMAc at 25 °C with an Ubbelohde viscometer. Wide-angle X-ray diffraction (WAXD) patterns were obtained at room temperature on a Rigaku D/MAX 2500 powder diffractometer with a scanning speed of 4°/min, and the patterns were recorded in the 2θ range of 5–40°. The solubility toward varied solvents of the obtained polymers was determined with 10 mg of a specimen in 1 mL of a solvent. The polymer thin films for stress–strain tests were cast from DMAc solutions onto glass plates, and this was followed by evaporation of the solvent and drying at 100 °C for 1 h, at 150 °C for 1 h, and at 200 °C in vacuum for 2 h. The tensile properties were performed on an Instron 3365 Tensile Apparatus with a 5 kg load cell at a crosshead speed of 5 mm/min. An average of at least five individual specimens was used for each sample. The dielectric constant was determined on an Agilent 4291B instrument at a frequency of 1 MHz to 1.1 GHz at 25 °C. The contact angle on the film for water was analyzed by an OCA40 Micro dynamic contact angle analysis system.

Monomer synthesis

*Synthesis of **2b–c***

Hydrochloric acid (11.8 M, 48 mL) and ice water (48 mL) were placed in a 500-mL beaker equipped with a mechanical stirrer, a dropping funnel, and a thermometer. Fluoroaniline monomer **1** (0.12 mol) was added dropwise into the stirred mixture through the dropping funnel, and then a concentrated water solution of sodium nitrite (8.28 g, 0.12 mol) was added dropwise. The mixture was stirred for 2 h at 0–5 °C and yielded a clear solution. The resulting solution was filtered and added dropwise to a mixture of 1,4-benzoquinone (11.66 g, 0.11 mol), sodium bicarbonate (20.41 g, 0.24 mol), and water (700 mL). The reaction was carried out at 8–12 °C for about 2 h and then at room temperature for another 2 h. The precipitate was collected by filtration, washed thoroughly with water, and dried at 60 °C in a vacuum oven. The product was recrystallized from *n*-butanol, and thus the yellow crystalline monomer was received.

The yield of **2b** was 80%. The characteristics of **2b** were as follows: melting point: 140 °C (DSC). m/z: 202. Elemental analysis, Calcd. for $C_{12}H_7FO_2$ (202.185 g/mol): C, 71.28%; H, 3.49%. Found: C, 71.24%; H, 3.41%. IR(KBr, v, cm^{-1}): 3061, 1658, 1604, 1512, 1454, 1341, 1299, 1241, 1166, 1105, 980, 920, 845. ^1H NMR ($CDCl_3$, δ, ppm): 7.49 (dd, $J = 8.8, 2.1$ Hz, 2H), 7.14 (t, $J = 8.6, 8.6$ Hz, 2H), 6.87 (d, $J = 8.4$ Hz, 1H), 6.85 (dd, $J = 8.5, 2.3$ Hz, 1H), 6.83 (d, $J = 2.0$ Hz, 1H).

The yield of **2c** was 90%. The characteristics of **2c** were as follows. Melting point: 128 °C (DSC). m/z:220. Elemental analysis, Calcd. for $C_{12}H_6F_2O_2$ (220.173 g/mol): C, 65.46%; H, 2.75%. Found: C, 65.37%, H, 2.69%. IR(KBr, ν, cm^{-1}): 3062, 1657, 1604, 1517, 1431, 1337, 1287, 1237, 1170, 1103, 1008, 885. ^1H NMR ($CDCl_3$, δ, ppm): 7.37 (m, 1H), 7.25 (dd, $J = 8.4, 2.7$ Hz, 1H), 7.24 (m, 1H), 6.89 (d, $J = 8.8$ Hz, 1H), 6.86 (dd, $J = 8.4, 2.2$ Hz, 1H), 6.83 (d, $J = 2.2$ Hz, 1H).

*Synthesis of **3b–c***

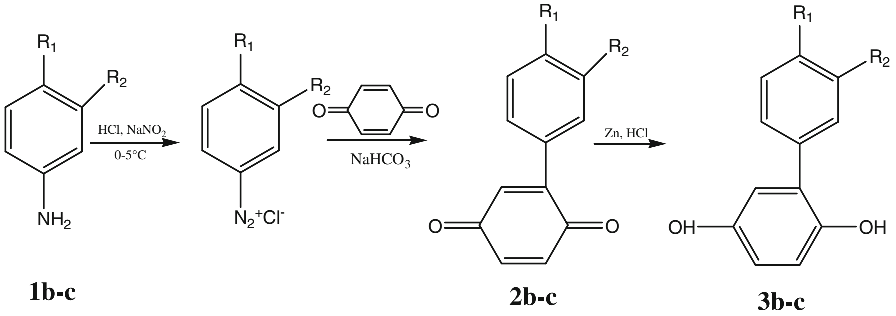
Intermediate **2** (0.05 mol), Zn powder (10.35 g, 0.15 mol), and 100 mL of deionized water were placed in a 250-mL, three-necked flask equipped with a mechanical stirrer, a condenser, and a dropping funnel. The mixture was heated to 95 °C with stirring, which was followed by the addition of 35 mL of HCl (11.8 M) dropwise at a rate of 0.5 drops per second. After complete addition, the reaction mixture was allowed to reflux for another 3 h. Then, the hot mixture was filtered. The filtrate was cooled to room temperature and poured into a large amount of deionized water. The white solid was collected.

The yield of **3b** was 65%. The characteristics of **3b** were as follows: melting point: 134 °C (DSC). m/z: 204. Elemental analysis, Calcd. for $C_{12}H_9FO_2$ (204.191 g/mol): C, 70.59%; H, 4.44%. Found: C, 70.55%; H, 4.37%. IR (KBr, ν, cm^{-1}): 3328, 3061, 1658, 1604, 1512, 1453, 1341, 1299, 1241, 1166, 1105, 980, 845. ^1H NMR ($CDCl_3$, δ, ppm): 7.44 (dd, $J = 8.8, 2.2$ Hz, 2H), 7.16 (t, $J = 8.8, 8.8$ Hz, 2H), 6.85 (d, $J = 8.8$ Hz, 1H), 6.75 (d, $J = 3.0$ Hz, 1H), 6.73 (dd, $J = 8.8, 3.0$ Hz, 1H), 4.68 (s, 1H), 4.48 (s, 1H).

The yield of **3c** was 63%. The characteristics of **3c** were as follows: melting point: 133 °C (DSC). m/z: 222. Elemental analysis, Calcd. for $C_{12}H_9FO_2$ (222.189 g/mol): C, 64.87%; H, 3.63%. Found: C, 64.78%; H, 3.60%. IR (KBr, ν, cm^{-1}): 3316, 1602, 1503, 1474, 1383, 1322, 1267, 1188, 1114, 950, 854. ^1H NMR ($CDCl_3$, δ, ppm): 7.56 (m, 1H), 7.40 (dd, $J = 8.0, 2.0$ Hz, 1H), 7.33 (m, 1H), 6.85 (d, $J = 8.6$ Hz, 1H), 6.81 (d, $J = 3.0$ Hz, 1H), 6.71 (dd, $J = 8.6, 3.0$ Hz), 3.21 (s, 1H), 3.19 (s, 1H).

Preparation of PAEKs

The general procedure for the preparation of the PAEKs **4a–c** was illustrated as follows by the example of **4b**. Bisphenol monomer **3b** (5 mmol), 1.09 g (5 mmol) of 4,4′-difluorobenzophenone, 0.83 g (6 mmol) of anhydrous K_2CO_3, 12 mL DMAc, and 10 mL toluene were placed in a 100-mL, three-necked flask equipped with a mechanical stirrer, a nitrogen inlet, a Dean-Stark trap and a condenser. The reaction mixture was allowed to reflux for 2 h at 165 °C. The toluene was removed by distillation through the Dean-Stark trap. The system was heated to 175 °C and maintained at this temperature until it became very viscous. The mixture was precipitated into 600 ml water with vigorous stirring followed by filtration. The resultant white solid polymer was washed thoroughly with hot water and then dissolved with chloroform and precipitated in methanol. After filtration, it was dried at 120 °C under vacuum overnight. The white solid polymer was obtained in a quantitative yield.



b: R_1:F, R_2: H; **c**: R_1:F, R_2: F

Scheme 1 Synthesis of bisphenol monomers

The characteristics of **4b** were as follows. Inherent viscosity (0.5 g/dL in DMAc, 25 °C): 0.50 dL/g. IR (film, v, cm^{-1}): 3060, 1660, 1600, 1480, 1230, 1160, 928, 839, 764. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.83 (d, $J = 8.6$ Hz, 1H), 7.78 (d, $J = 8.6$ Hz, 1H), 7.73 (d, $J = 8.6$ Hz, 1H), 7.68 (d, $J = 8.6$ Hz, 1H), 7.45 (t, $J = 6.5$, 6.5 Hz, 2H), 7.19–7.08 (m, 5H), 7.02 (t, $J = 8.5$, 8.5 Hz, 2H), 6.92 (t, $J = 8.1$, 8.1 Hz, 2H). ^{19}F NMR ($CDCl_3$, δ, ppm): −113.82 (s, 1F).

Results and discussion

Monomer synthesis

As shown in Scheme 1, the bisphenol monomers **3b** and **3c** were synthesized in two steps by the coupling reaction of (4-fluorophenyl)diazonium chloride and (3,4-difluorophenyl)diazonium chloride with 1,4-benzoquinone in the presence of $NaHCO_3$ to yield **2b** and **2c**, respectively, followed by reduction with Zn/HCl.

The structures of **2b**–**c**, and **3b**–**c** were confirmed by IR and ^{1}H NMR spectra. In the IR spectra (Fig. 1), **2b** showed an absorption band around 1660 cm^{-1} due to symmetric stretching of carbonyl groups. After reduction, this characteristic absorption disappeared, and the characteristic bands of hydroxyl groups around 3330 cm^{-1} appeared. Furthermore, the peaks at 4.50–5.00 ppm in ^{1}H NMR spectrum of **3b** (Fig. 2) were assigned to the hydroxyl protons, which were absent in the spectrum of **2b**. All of these illustrated that the carbonyl groups of **2b**–**c** had been reduced to the hydroxyl groups. The assignments of each proton are given in the Fig. 2, and this spectrum agree well with the proposed molecular structure of **3b**.

Polymer synthesis

The polymerizations of bisphenol monomers and 4,4′-diflourobenzophenone were carried out in the presence of excess potassium carbonate as a base in the mixture of DMAc and toluene, as shown in Scheme 2. The bisphenolate formation was processed at 165 °C and the water generated from deprotonation of the bisphenols

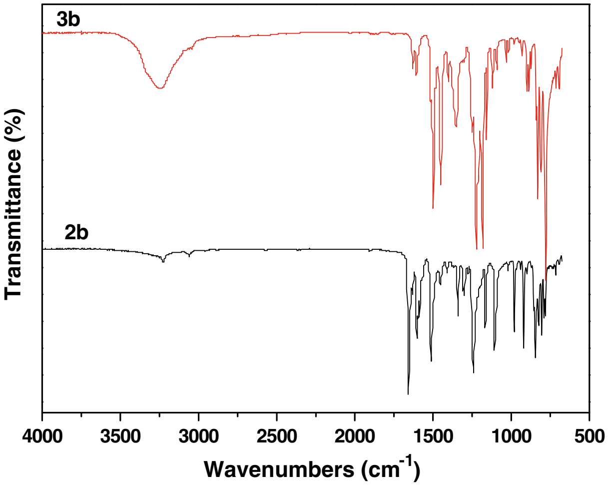


Fig. 1 FTIR spectra of **2b** and **3b**

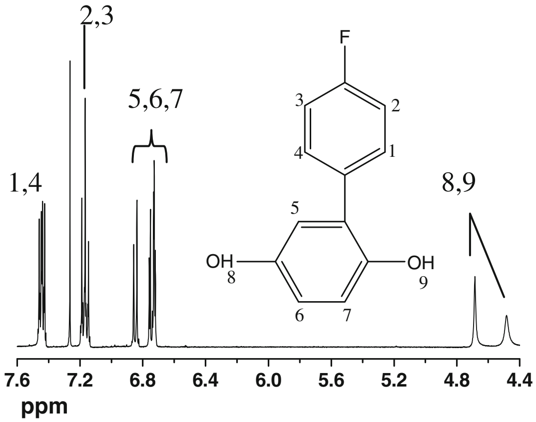


Fig. 2 ^{1}H NMR spectra of **3b**

was removed by toluene through the Dean-Stark trap. Then the temperature was increased to 175 °C, and homogeneous, transparent, viscous polymerization solution was produced. White, fibrous polymer was obtained when the resultant polymer solution was poured into an excess deionized water. The resulting polymers had high inherent viscosities of 0.50–0.92 dL/g in DMAc solution at 25 °C (Table 1).

The chain structure of the PAEKs was confirmed by FTIR and NMR spectra. In FTIR spectra, all the polymers exhibited the characteristic absorption bands around 1230 cm^{-1} due to aryl ether linkages and around 1660 cm^{-1} corresponding to aryl carbonyl groups. There was also a peak around 1160 cm^{-1} which was based on C–F bond of fluorinated PAEKs. In addition, the characteristic absorption bands of the hydroxyl groups at the 3330 cm^{-1} disappeared after polymerization. The representative of FTIR spectrum of PAEK **4b** is illustrated in Fig. 3.

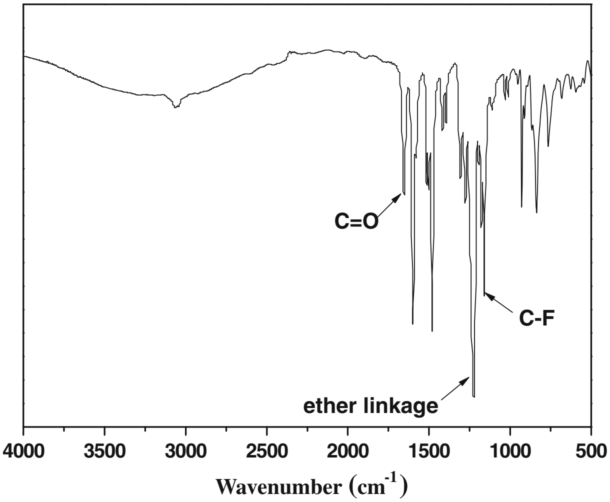
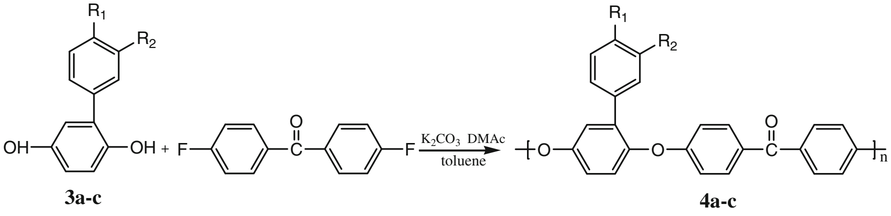


Fig. 3 FTIR spectra of **4b**



a: R_1-H, R_2-H; **b**: R_1-F, R_2-H; **c**: R_1-F, R_2-F

Scheme 2 Synthesis of PAEKs

Table 1 Inherent viscosity and thermal properties of PAEKs **4a–c**

Polymer	η_{inh} (dL/g)	Td_5 (°C)	Td_{10} (°C)	T_g (°C)
4a	0.69	527	544	160
4b	0.50	575	587	153
4c	0.92	587	606	148

[a] Measured at a concentration of 0.5 g dL^{-1} in DMAc at 25 °C

In the ^1H NMR and ^{19}F NMR spectra of PAEKs, the assignments were in good agreement with the proposed structures. The signals at 6.91–7.84 ppm in ^1H NMR spectra were assigned to the aromatic protons in the polymers backbone. The sharp peaks near 4.5 ppm corresponding to the hydroxyl protons in ^1H NMR were absent, which supported the complete deprotonation proceeded in the polycondensation. A single peak was observed at −113.82 ppm in the ^{19}F NMR spectrum of **4b** (Fig. 4), and there were two peaks around −137.39 and −138.28 ppm, respectively, in the ^{19}F NMR spectrum of **4c** (Fig. 5).

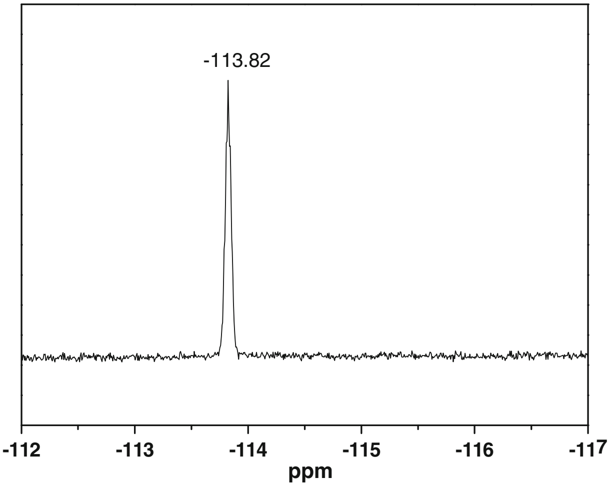


Fig. 4 ^{19}F NMR spectra of **4b**

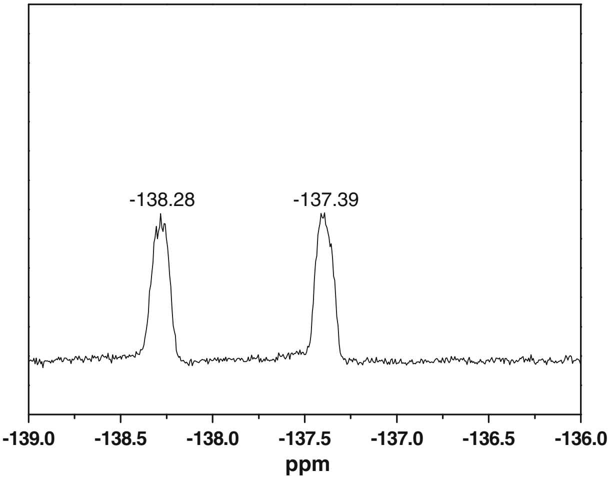


Fig. 5 ^{19}F NMR spectra of **4c**

The crystallinity of the PAEKs was evaluated by wide-angle X-ray diffraction (Fig. 6). They all exhibited amorphous patterns. This could be attributed to bulky pendant groups which disrupted the regularity of molecular chains and inhibited the close packing of the polymer chains.

Thermal properties

The thermal behavior of these PAEKs was summarized in Table 1. No melting endotherms were observed from DSC curves (Fig. 7a), which further confirmed the amorphous nature of the obtained PAEKs. The T_g values of these PAEKs were read

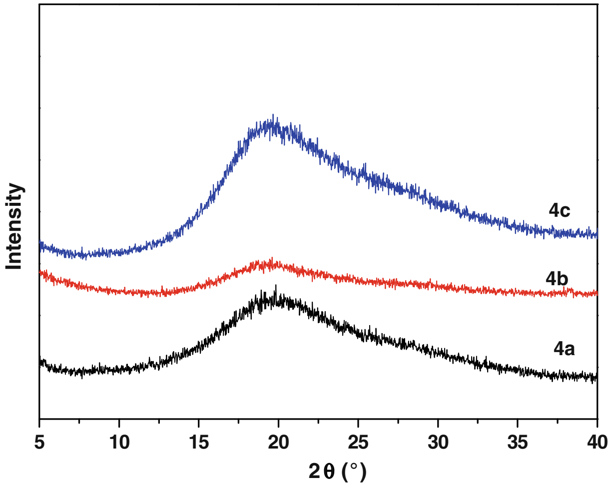
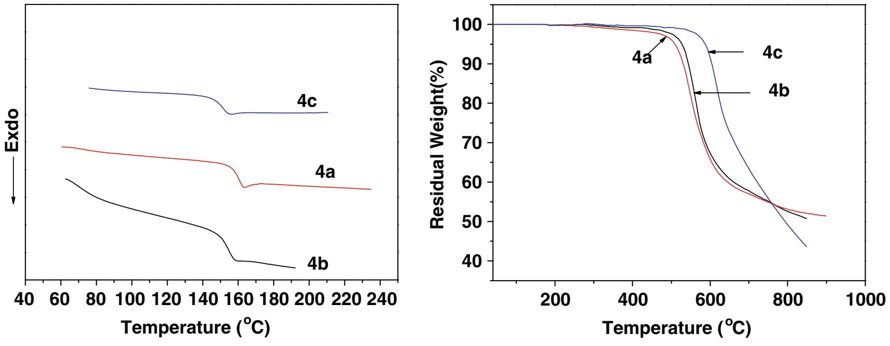


Fig. 6 Wide-angle X-ray diffractograms of **4a–c**



(a) (b)

Fig. 7 DSC (**a**) and TGA (**b**) curves of PAEKs

from the DSC curves. Although the T_g showed some decrease because of the incorporation of fluorine-contained groups, the values of T_g were still above 148 °C. Compared with the (3-trifluoromethyl)phenyl-substituted PAEKs [26], PAEKs **4a–c** exhibited higher T_g values. A possible explanation is that the incorporation of fluorine would lead to an internal plasticization in addition to the geometry and free-volume factors [29], and the larger the fluorine content the greater the effect, thus the lower T_g values were observed (Fig. 7b).

The TGA results indicated that all the PAEKs exhibited good thermal stability. The temperatures at 5% weight loss (Td_5) were above 527 °C and the temperatures at 10% weight loss (Td_{10}) were above 544 °C in nitrogen. As anticipated, fluorinated polymers showed a higher thermal stability than the corresponding nonfluorinated polymer. This could be attributed to the stronger C–F bond in comparison with C–H bond [26]. So, these PAEKs possessed sufficiently high T_g

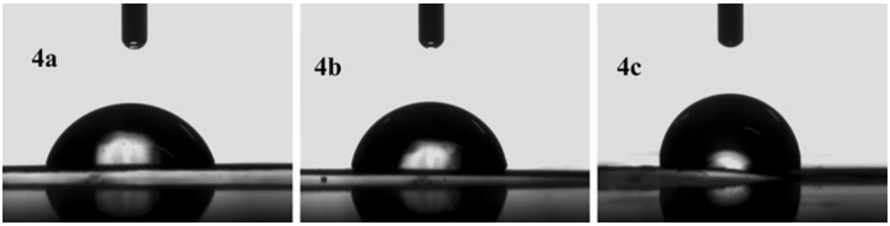


Fig. 8 Surface contact angle for water of PAEKs

Table 2 Solubility of the obtained PAEKs

Polymers	$CHCl_3$	DMSO	NMP	DMF	DMAc	THF	H_2SO_4
4a	++	+−	++	++	++	++	++
4b	++	+−	++	++	++	++	++
4c	++	++	++	++	++	++	++

10 mg sample in 1 mL solvent

++, Soluble at room temperature; +−, soluble on heating; –, insoluble. $CHCl_3$, chloroform; DMSO, dimethyl sulfoxide; NMP, *N*-methyl-2-pyrrolidone; DMF, *N*,*N*-dimethylformamide; DMAc, *N*,*N*-dimethylacetamide; THF, tetrahydrofuran; H_2SO_4, concentrated sulfuric acid

Table 3 Mechanical properties, dielectric constants, and contact angles of PAEKs

Polymers	Tensile strength (MPa)	Young’s modulus (GPa)	Elongation at break (%)	Dielectric constant (at 1 MHz)	Contact angle for water θ(°)
4a	104.0	2.68	15	2.95	83.9
4b	98.3	2.74	27	2.82	90.3
4c	95.2	3.06	32	2.75	98.4

and excellent thermal stability which could withstand the soldering and processing temperatures as insulating material for microelectronics.

Solubility and mechanical properties

Conventional PAEKs without side groups could not be dissolved in most common organic solvents. While as expected, the obtained PAEKs in this study showed good solubility and could readily dissolve in $CHCl_3$, DMF, NMP, DMAc, and THF at room temperature (Table 2). The excellent solubility could be attributed to the presence of bulky pendant groups, which decreased the packing density and intermolecular interaction of macromolecular chain, thereby enhanced solubility.

All the obtained PAEKs could form transparent, strong, and flexible films by casting of their polymer solutions. The mechanical properties of these PAEKs films were summarized in Table 3. The tensile strengths, Young’s moduli and elongations at break of these PAEKs were in the range of 95.2–104.0 MPa, 2.68–3.06 GPa, and 15–32%, respectively.

Dielectric constant and contact angle for water

The dielectric constants of the obtained PAEKs, as listed in Table 3, were measured on the films. At 1 MHz, the dielectric constant of conventional PAEK without pendant groups was 3.3. The dielectric constants of the PAEKs decreased when the bulky phenyl pendant groups were incorporated into the polymer chains. Two related factors could be used to explain the effect of bulky pendant groups on the dielectric properties of polymers. First, the bulky side groups might have pushed the neighboring chains apart, and this resulted in loosely packed polymer chains and a low dielectric constant. Second, the bulky pendant groups interrupted the regular packing of the polymer chains, which disrupted the crystallinity and decreased the dielectric constant of the polymer. Furthermore, with the increase of the content of fluorine, the dielectric constants decreased**,** which was attributed to the strong electronegativity and low polarizability of fluorine.

The contact angles (θ) for water on the films of the obtained PAEKs were presented in Table 3 (Fig. 8). The θ gradually increased with the increase of fluorine, which indicated the increase in hydrophobicity due to the introduction of fluorophenyl groups.

Conclusion

PAEKs with fluorophenyl side groups have been successfully synthesized from two new bisphenol monomers. The obtained PAEKs had good solubility in many common solvents at room temperature. Meanwhile, they showed high T_g values and high thermal stability. Compared with the non-fluorinated PAEK **4a**, the fluorinated PAEKs **4b–c** displayed lower dielectric constants and higher hydrophobicity. The excellent combination of several important properties made the obtained PAEKs promising materials for microelectronic application.

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