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Synthesis and Properties of Poly(Aryl Ether Ketone) Copolymers with Trifluoromethyl-Substituted Benzene in the Side Chain

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The new monomer (4-(4'-trifluoromethyl)phenoxyphenyl)hydroquinone (TFPOPH) was synthesized in a three-step synthesis. A series of poly(aryl ether ketone) copolymers were prepared by the reaction of (4-(4'-Trifluoromethyl)phenoxyphenyl)hydroquinone and hydroquinone (HQ) with 4,4'-difluorobenzophenone (DFB) in the presence of potassium carbonate in tetramethylene sulfone (TMS). Thermal analyses of the fluorinated copolymers showed that the glass transition temperature and 5.0% weight loss temperature are similar with that of PEEK, and the crystallinity decreased with increasing of TFPOPH. For the copolymer synthesized with the molar fraction of TFPOPH in the diphenol monomers (TFPOPH, HQ) being over 0.2, no cold crystallization temperature and melting temperature were detected, indicating that these copolymers are almost amorphous. The crystal structure of the copolymers with the molar fraction of TFPOPH being not higher than 0.2 is rhombic. The solubility in polar aprotic solvents of poly(aryl ether ketone)s copolymers increases and dielectric constant decreases step by step.

Keywords poly(aryl ether ketone), fluoropolymers, dielectric properties

Introduction

Poly (aryl ether ketone)s (PAEK) are known as one of the high-performance semicrystalline engineering thermoplastics due to their outstanding thermal and mechanical properties (1–3). Since high molecular weight poly(ether ether ketone) (PEEK), the most popular member of poly(aryl ether ketone)s (PAEKs), was developed by ICI in 1977, it has been extensively used in electrical, automotive, aerospace, oil and chemical industries owing to excellent mechanical properties, good solvent resistant, size-accuracy and electrical characteristics and superior thermal stability (4, 5). In recent years, considerable attention has been devoted to the preparation of fluorine-containing polymers due to their unique properties and high-temperature performance. The incorporation of fluorine

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atoms (or groups containing fluorine atoms) into polymer chains changes solubility of polymers, glass transition temperature (T_g) and thermal stability, while also leading to decreased moisture absorption and dielectric constant. The aromatic fluoropolymers have currently been used as films, coatings microelectronics devices (6–12). In this paper, we report the synthesis of novel fluorine-containing PAEK copolymers with 4-(4'-trifluoromethyl)phenoxyphenyl moieties via aromatic nucleophilic substitution reaction.

Experimental

Materials

4-chlorobenzotrifluoride and 4-aminophenol were obtained from Beijing Chemical Reagents Corporation. 4,4'-Difluorobenzophenone (purity 98%, industrial grade) and hydroquinone (HQ) (purity 98%, industrial grade) which were obtained from Yanji Chemical Plant, China, were dried *in vacuo* at 70°C for 8 h. Potassium carbonate (purity 99%, analysis reagent, Tianjin Chemical Reagent Plant, China) was dried at 110°C for 6 h. The other reagents also were used as received.

Monomer Synthesis

4-(4'-Trifluoromethyl)phenoxy Aniline. To a 500 mL round-bottom flask were added 24.0 g (0.22 mol) of 4-aminophenol and 14.0 g (0.25 mol) of KOH, 100 mL of toluene and 200 mL of DMSO. The mixture was heated to 140°C with stirring under nitrogen for 3 h to remove produced water by azeotropic distillation with toluene. After complete removal of the water, the residual toluene was distilled off. Then, the solution was cooled to 100°C and 28 g (0.15 mol) of 4-chlorobenzotrifluoride in 40 mL of DMSO were added dropwise. The reaction was carried out with stirring at 120°C for 8 h, and then the mixture was poured into 1000 mL of cold water to give a precipitate. The pale brown solid was collected and washed thoroughly with water to give a crude product that was purified by recrystallization in ethanol/water.

(Yield: 80%. m.p. 78–80°C (DSC). $m/z = 253$. Elem. Anal. $C_{13}H_{10}F_3NO$ Calcd. C 61.66, H 3.98, N 5.53; Found. C 61.45, H 3.84, N 5.21. IR (KBr, cm^{-1}): 3402 (Ar-NH₂), 1624 (vs, C=C), 1510 (vs, C=C), 1333 (C-F), 1254 (vs, C-O), 1107 (vs, C-O), 841 (C-H). ¹H NMR (CDCl₃, δ , ppm): $\delta = 7.51$ (d, $J = 8.5$ Hz, 2H), 6.96 (d, $J = 8.5$ Hz, 2H), 6.89 (d, $J = 8.5$ Hz, 2H), 6.73 (d, $J = 8.5$ Hz, 2H), 3.92 (s, 2H). ¹³C NMR (CDCl₃, δ , ppm) $\delta = 161.73$, 147.99, 142.35, 127.01, 125.42, 121.62, 121.10, 118.10, 116.93(q, $J = 88$ Hz, -CF₃)

4-(4'-Trifluoromethyl)phenoxyphenyl)benzoquinone. Into a 2000 mL beaker equipped with a mechanical stirred, a dropping funnel and a thermometer were placed hydrochloric acid (11.8 M, 340 mL), water (200 mL) and ice (200 g). 4-(4'-trifluoromethyl)phenoxy aniline (253 g, 1.0 mol) was added dropwise into the stirred mixture through the dropping funnel, and then a concentrated water solution of sodium nitrite (69 g, 1.0 mol) was added dropwise. The mixture was stirred for 2 h at 0–5°C and yields a clear solution.

The resulting solution was filtered and added dropwise to a mixture of 1,4-benzoquinone (108 g, 1.0 mol), sodium bicarbonate (252 g, 3.0 mol), and water (500 mL). The reaction mixture was stirred at 8–12°C for 2 h and then at room temperature for 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 produced yellow crystals.

(Yield: 80%. m.p. 78–80°C (DSC). $m/z = 344$. Elem. Anal. $C_{19}H_{11}F_3O_3$ Calcd. C 66.28, H 3.22; Found. C 66.50, H 3.16. IR (KBr, cm^{-1}): 1641 (vs, C=C), 1508 (vs, C=C), 1333 (C-F), 1258 (vs, C-O), 1068 (vs, C-O), 858 (C-H). 1H NMR ($CDCl_3$, δ , ppm): $\delta = 7.62$ (d, $J = 8.5$ Hz, 2H), 7.52 (d, $J = 8.5$ Hz, 2H), 7.12 (d, $J = 9.0$ Hz, 2H), 7.09 (d, $J = 9.0$ Hz, 2H), 6.89–6.83 (m, 3H). ^{13}C NMR ($CDCl_3$, δ , ppm) $\delta = 187.46$, 186.70, 159.37, 158.01, 144.92, 141.90, 138.29, 137.05, 136.38, 132.21, 131.24, 129.35, 128.40, 127.36, 118.74 (q, $J = 88$ Hz, $-CF_3$)

(4-(4'-Trifluoromethyl)phenoxyphenyl)hydroquinone (TFPOPH). (4-(4'-Trifluoromethyl)phenoxyphenyl)benzoquinone (172 g, 0.50 mol), Zn powder (98.1 g, 1.50 mol), and 400 mL of deionized water were placed into a 1000 mL, three-necked flask equipped with a mechanical stirrer, a condenser, and a dropping funnel. The mixture was heated to 90°C with stirring, which was followed by the addition of 120 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 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 off-white solid was collected and recrystallized from toluene.

(Yield: 80%. m.p. 75–77°C (DSC). $m/z = 346$. Elem. Anal. $C_{24}H_{13}F_3O_3$ Calcd. C 65.90, H 3.78; Found. C 77.47, H 3.73. IR (KBr, cm^{-1}): 3406 (s, OH), 1604 (vs, C=C), 1500 (vs, C=C), 1327 (C-F), 1244 (vs, C-O), 1114 (vs, C-O), 835 (C-H). 1H NMR ($CDCl_3$, δ , ppm): $\delta = 7.71$ (d, $J = 8.5$ Hz, 2H), 7.52 (d, $J = 8.5$ Hz, 2H), 7.13 (d, $J = 9.0$ Hz, 2H), 7.09 (d, $J = 9.0$ Hz, 2H), 6.79–6.70 (m, 3H). ^{13}C NMR ($CDCl_3$, δ , ppm) $\delta = 159.30$, 156.03, 150.46, 149.20, 137.80, 127.52, 126.00, 125.31, 124.45, 123.49, 123.27, 120.21, 118.20 (q, $J = 88$ Hz, $-CF_3$), 117.62, 116.53.

Synthesis of the Copolymers Containing 4-(4'-Trifluoromethyl)phenoxyphenyl Moieties

To a three-neck round bottom flask were added hydroquinone and (4-(4'-trifluoromethyl)phenoxyphenyl)hydroquinone (TFPOPH) (total 0.10 mol) in molar ratios of 100:0, 80:20, 60:40, 40:60, 20:80 or 0:100, 4,4'-difluorobenzophenone (DFB), toluene and 3.04 g (0.022 mol) of potassium carbonate and tetramethylene sulfone (TMS) (a prescribed amount shown in Table 2) and heated to 140°C to remove produced water by azeotropic distillation with toluene and then rose up to 210°C for 4–6 h. The mixture was cooled to room temperature. The copolymer was precipitated by pouring the hot reaction mixture into a large amount of distilled water, filtered, and washed with acetone and distilled water several times. Drying at 120°C for 12 h afforded an off-white polymer in 90–95% yield.

Measurements

Glass transition temperatures (T_g) reported in this article were determined using Mettler Toledo DSC 821e differential scanning calorimetry (DSC). The heating rate was 20°C/min. In all experiments, the original samples were heated from 80°C to 400°C. The values of the glass transition temperature T_g were taken as the temperature of the midpoint of the increment of the specific heat capacity. Thermal gravimetric analyses (TGA) were determined in air using a heating rate of 20°C/min and polymers were contained within open aluminum pans on a Perkin-Elmer TGA-7.

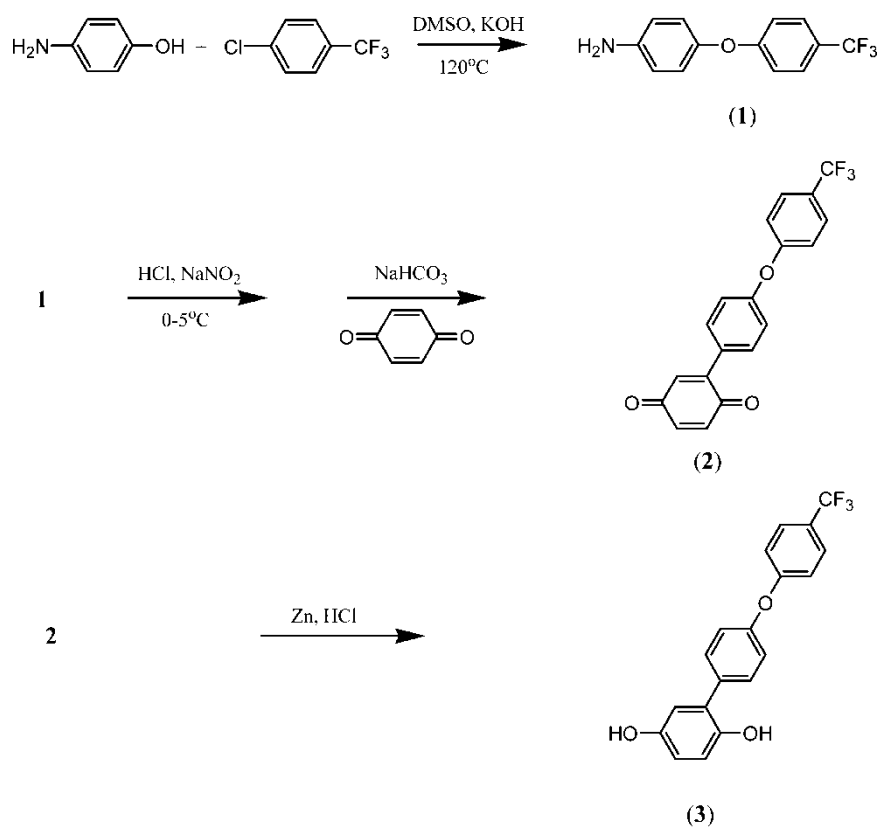
Infrared spectral analysis was performed on a Nicolet Impact410 FTIR using the polymer films. ^1H (500 MHz) and ^{13}C (125 MHz) spectra were recorded in CDCl_3 solutions on a Bruker 510 MHz NMR, and the result was reported in ppm from tetramethylsilane in the δ scale.

Wide-angle X-ray diffraction patterns were recorded in the reflection mode at room temperature by using a Rigaku D/max-rA. Graphite monochromator and $\text{CuK}\alpha$ radiation were used. The diffractometer was equipped with a $\theta - 2\theta$ goniometer, the diffraction scans were collected at 2θ between 4 and 50° for the polymer films. Inherent viscosities of the copolymers were measured at 25°C on a 0.1 g/dL solution in 98% sulfuric acid (13). The dielectric constants were measured on an HP 1645 B/4194A impedance gain-phase analyzer with a round-board electrode. The measured copolymers films of 1.0 mm thickness and 10.0 mm width were made by compression molding and then quenching in ice water.

Results and Discussion

Synthesis of Monomer

The synthesis of the three fluorine-containing diphenol is shown in Scheme 1. TFPOPH was synthesized by reducing the diquinone compound 2 that were derived from



Scheme 1. Synthesis of monomer, (4-(4'-trifluoromethyl)phenoxyphenyl)hydroquinone.

1,4-benzoquinone with compound 1. The chemical structure of TFPOPH was confirmed by elemental analysis, FTIR, NMR and MS.

Synthesis of the Copolymers Containing 4-(4'-Trifluoromethyl)phenoxyphenyl Side Chain

Scheme 2 outlines the synthesis of poly(aryl ether ketone)s copolymers derived from different molar ratio of TFPOPH and hydroquinone with 4,4'-difluorobenzophenone by the nucleophilic substitution reaction method. The polymerizations were completed at a solid content of about 20%, and toluene was used for the azeotropic removal of water.

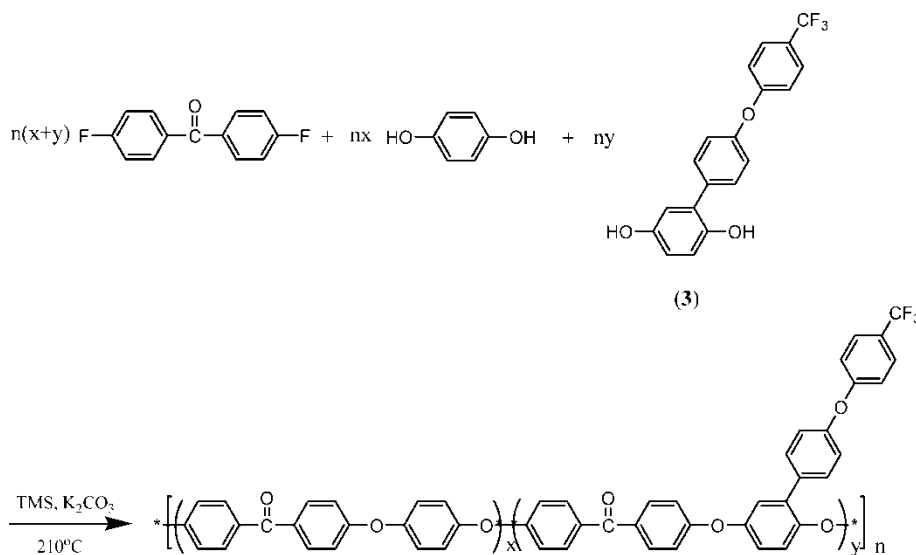
After the completion of bisphenolate formation in about 2 h, the reaction temperature was increased to 220°C. High molecular weight polymers were readily obtained in 4–6 h. The resulting copolymers had high inherent viscosities of 0.52–0.95 dL/g (Table 2).

Copolymer Solubility

The solubility of the PAEK copolymers is listed in Table 1 that was qualitatively determined by mixing 1.5 g of solid with 8.5 g of organic solvents, followed by stirring in nitrogen for 24 h to determine if the solid was completely or partly dissolved in organic solvents. The solubility of poly(aryl ether ketone)s copolymers increased following increasing content of 4-(4'-trifluoromethyl)phenoxyphenyl side chain. The excellent solubility of these PAEKs could be attributed to the presence of bulky pendant groups, which led to increased free volume and broken crystallinity of polymers.

Thermal Behaviors

Figure 1 shows the DSC traces of the quenched samples of the copolymers in the heating run. When the molar fraction of TFPOPH is over 0.2, the clear cold-crystallization temperature (T_c) and T_m cannot be detected. For the copolymer samples with a



Scheme 2. Synthesis of the copolymers containing 4-(4'-trifluoromethyl)phenoxyphenyl moieties.

Table 1
Solubility of PAEK copolymers containing trifluoromethyl-substituted benzene in the side chain

No.	Molar fraction of TFPOPH	Solvent					
		DMF	DMAc	NMP	THF	CH ₂ Cl ₂	Acetone
1	0.00	–	–	–	–	–	–
2	0.20	–	–	–	–	–	–
3	0.40	+	+	+	–	–	–
4	0.60	+	+	+	±	±	–
5	0.80	++	++	++	+	+	–
6	1.00	++	++	++	++	++	–

++, soluble at room temperature; +, soluble on heating; ±, swelling on heating; –, insoluble.

TFPOPH molar fraction of not more than 0.2, the T_m decreased with increasing the content of TFPOPH, while T_c showed the reverse tendency. These results are thought to be attributed to the disturbance of the segmental movement and the destruction of the symmetry and regularity of the molecular chains due to the introduction of 4-(4'-trifluoromethyl)phenoxyphenyl pendant group. The glass transition temperature (T_g) increased and then decreased with increasing the content of TFPOPH moieties. One possible explanation for the change is the affection of molecule weight (14, 15), the other is that the introduction of bulky pendant group would block the mobility of segments and the atom of fluorine would lead to an internal plasticization in addition to the geometry and free-volume factors (16).

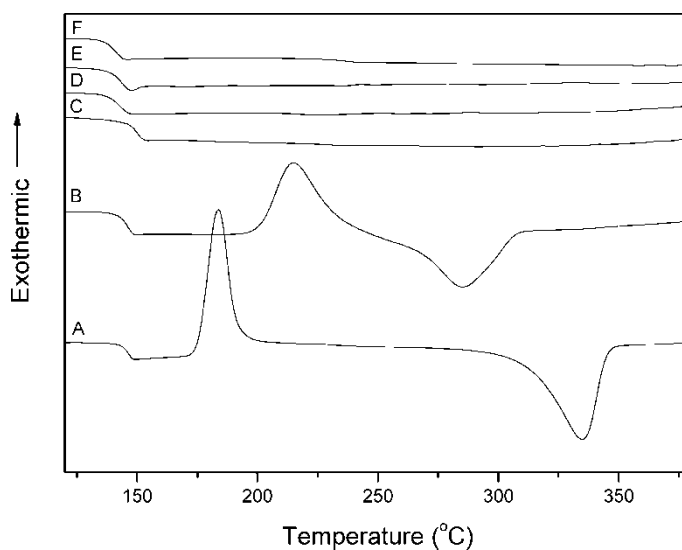


Figure 1. DSC traces of PAEK copolymers containing trifluoromethyl-substituted benzene. (A) 0.00, (B) 0.20, (C) 0.40, (D) 0.60, (E) 0.80, (F) 1.00.

Table 2
Experimental data and properties of PAEK copolymers containing trifluoromethyl-substituted benzene in the side chain

No.	DFB (mol)	HQ (mol)	TFPOPH (mol)	Molar fraction of TFPOPH ^a	T _g (°C)	T _m (°C)	T _d ^b (°C)	η _{inh} ^c (dL/g)
1	0.10	0.10	0.00	0.00	143	334	561	0.79
2	0.10	0.08	0.02	0.20	145	284	531	0.56
3	0.10	0.06	0.04	0.40	149	—	575	0.95
4	0.10	0.04	0.06	0.60	146	—	555	0.68
5	0.10	0.02	0.08	0.80	142	—	573	0.52
6	0.10	0.00	0.10	1.00	140	—	553	0.54

^aMolar ratio of TFPOPH/(TFPOPH + HQ).

^bT_d is the temperature at which the weight loss of the polymer is 5.0%.

^cMeasured at the concentration of 0.1 g/dL solution in 98% sulfuric acid at 25°C.

The 5.0% weight loss temperatures (T_d) of the copolymers were determined by thermogravimetric analysis given in Table 2. The copolymers with a TFPOPH molar fraction of 0.20 showed the T_d (531°C), which is little lower than that of PEEK (561°C). However, the copolymers sustained the T_d over 530°C.

Wide-angle X-ray Diffraction Analysis

The results of WAXD measurement of PEEK and the copolymers are shown in Figure 2. The pattern of diffraction peaks and the values of 2θ for each diffraction peak are the same as each other, suggesting that the crystal structure of the copolymer is a rhombic system in the same manner as is PEEK (17). The intensity of diffraction peaks decreased with

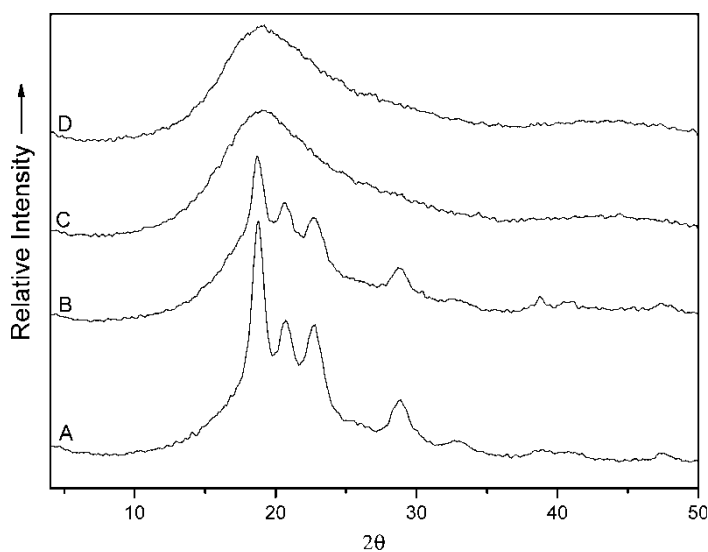


Figure 2. WAXD patterns of the copolymers with the molar fraction of 1,5-BFPN. (A) 0.00, (B) 0.20, (C) 0.40, (D) 0.60.

Table 3
Dielectric constant of PAEK copolymers containing trifluoromethyl-substituted benzene in the side chain

Molar fraction of TFPOPH	0.0	0.2	0.4	0.6	0.8	1.0
Dielectric constant (at 1 MHz)	3.30	3.22	3.00	2.87	2.72	2.67

increasing content of TFPOPH moieties. It can therefore be presumed that the segments containing TFPOPH moieties in the copolymer are not in the crystal unit cell of the copolymer but in the amorphous phase between the crystalline lamellae.

Dielectric Constants and Water Sorption

The dielectric constants of the copolymers, as listed in Table 3, were measured on the thin films. At 1 MHz, the dielectric constant of conventional PEEK without pendant groups was 3.3. The dielectric constants of the copolymers decreased when the bulky 4-(4'-trifluoromethyl)phenoxyphenyl increased. There is a related factor that the pendant groups may affect the dielectric properties of the polymers. The bulky side groups attached to the polymer main chains might have pushed the neighboring chains apart, and this resulted in loosely packed polymers and a low dielectric constant. By the same token, the incorporation of bulky pendant groups disrupted the crystallinity, leading to a less dense amorphous structure and a decreased dielectric constant.

Conclusions

The new fluoro-containing aromatic bisphenol monomer, (4-(4'-trifluoromethyl)phenoxyphenyl)hydroquinone, was synthesized and characterized. A series of fluorine-containing poly(aryl ether ketone) copolymers were synthesized by aromatic nucleophilic substitution reactions. The copolymers showed good solubility and low dielectric constant with increasing content of TFPOPH moieties.

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