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FLUORENE-BRIDGED POLYPHENYLQUINOXALINES WITH HIGH SOLUBILITY AND GOOD THERMAL STABILITY: SYNTHESIS AND PROPERTIES*

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Abstract A novel fluorene-bridged tetraketone monomer, 9,9-bis[(4-benzilyloxy)phenyl]fluorene (FLTK) was synthesized and characterized. The tetraketone was polymerized with various aromatic tetraamines to afford a series of polyphenylquinoxalines (PPQs). The obtained polymers were found to be soluble in common organic solvents such as *N*-methyl-2-pyrrolidone (NMP), chloroform and *m*-cresol. Flexible and tough PPQ films obtained by spin-casting their NMP solutions exhibited tensile strengths higher than 60 MPa. The films also demonstrated good thermal stability up to 500°C in nitrogen and glass transition temperatures higher than 280°C. In addition, the PPQ films exhibited good hydrolytic stability. High surface and volume resistivity retentions were achieved for the films after immersion or boiling in water for 24 h.

Keywords: Polyphenylquinoxaline; Fluorene; Solubility; Thermal stability; Hydrolytic stability.

INTRODUCTION

Over the past decades, there has been an increasing interest in developing fluorene-containing polymers for a variety of applications including low dielectric constant dielectrics for integrated circuit fabrication[1, 2], proton exchange membranes for advanced fuel cells[3, 4] and high refractive index coatings for advanced optical devices[5–7]. Generally, the fluorene-bridged polymers are characterized by their good thermal stability, enhanced solubility in common organic solvents (thus good processability) as well as many desirable optical and dielectric properties due to the bulky, amorphous and fused ring structure of the fluorene unit[8–13]. Thus, when designing high performance polymers for advanced applications, fluorene is often one of the most optimal groups.

Polyphenylquinoxaline (PPQ) is an important class of heteroaromatic polymers and has been widely investigated as high-temperature resistant coatings for extreme applications since its first report in 1967[14–17]. However, the high cost of conventional PPQs derived from aromatic tetraketone and tetraamine monomers greatly restricted their applications in high-tech fields. Thus, numerous methods aiming at reducing the costs of PPQs either by utilizing self-polymerizable monomers containing preformed quinoxaline units[18–20] or modifying the conventional synthetic procedure of aromatic tetraketone monomers[21, 22] have been developed in the literature. Recently, we noticed a route for the synthesis of aromatic ether-containing tetraketones *via* the nucleophilic substitution reactions of cheap 4-nitrobenzil and easily-available aromatic bisphenols[23]. This route notably enriches the species of tetraketone monomers; thus, expands the functionality and applications of PPQs.

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However, the tetraketones derived by this route inevitably contain flexible ether linkages, which might decrease the glass transition temperatures (T_gs) of the derived PPQs. We have tried to increase the T_g values of the ether-PPQs by introducing *ortho*-substituted methyl groups so as to prohibit the internal rotation around the ether linkages due to the steric effects of the methyl substituents[24]. The derived PPQs exhibited high T_g values exceeding 280°C. However, the thermal decomposition temperatures decreased dramatically due to the unstable nature of methyl groups at the elevated temperatures.

Then, in the present work, the bulky fluorene groups were introduced into ether-PPQs aiming at increasing the T_g values of PPQs while maintaining their inherent thermal stability. For this purpose, a novel tetraketone monomer, 9,9-bis[(4-benzilyloxy)phenyl]fluorene (FLTK) was synthesized first. Then, the tetraketone was polymerized with four aromatic tetraamines to afford a series of PPQs. The effects of fluorene structure on the solubility, thermal stability, hydrolytic stability and glass transition behavior of the PPQs were investigated.

EXPERIMENTAL

Materials and Characterization

9,9-Bis(4-hydroxyphenyl)fluorene (TCI, Japan) and 3,3′,4,4′-tetraaminobiphenyl (Acros, USA) were purchased and used as received. 3,3′,4,4′-Tetraaminodiphenyl ether[25], 3,3′,4,4′-tetraaminodiphenyl sulfone[26], 2,6-bis[(3,4-diamino)phenyl]-4′-phenylpyridine[27] and 4-nitrobenzil[28] were synthesized in our laboratory according to the corresponding literature. Dimethylsulfoxide (DMSO), *N*-methyl-2-pyrrolidinone (NMP), *N,N*-dimethylacetamide (DMAc) and *m*-cresol were purified by distillation prior to use. The other commercially available reagents were used without further purification. Inherent viscosity was measured using an Ubbelohde viscometer with a 0.5 g/dL NMP solution at 30°C. FT-IR spectra were obtained with a Tensor 27 Fourier transform spectrometer. UV-Vis spectra were recorded on a Hitachi U-3210 spectrophotometer at room temperature. Prior to test, PPQ films were dried at 100°C for 1 h to remove the absorbed moisture. ^{1}H-NMR and ^{13}C-NMR were performed on an AV 400 spectrometer operating at 300 MHz in DMSO-d_6 or $CDCl_3$. Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) were performed on a TA-Q series thermal analysis system at a heating rate of 10 K/min and 20 K/min in nitrogen, respectively. The tensile properties were performed on an Instron 3365 Tensile Apparatus with 80 mm × 10 mm × 0.05 mm specimens in accordance with GB1447-83 at a drawing rate of 2.0 mm/min. The electrical insulation properties were measured on a ZC36 Precision Resistivity Meter. The surface resistivity (ρ_s) and volume resistivity (ρ_v) of PPQ films were measured with 50 mm × 50 mm × 0.05 mm samples. The samples were dried at 120°C for 1 h prior to measurement. Solubility was determined as follows: 1.0 g of the tested PPQ resin was mixed with 9.0 g of the solvent at room temperature (10 wt% solid content), which was then mechanically stirred under nitrogen for 24 h. The solubility was determined visually as three grades: completely soluble (++), partially soluble (+), and insoluble (–). The complete solubility is defined as a homogenous and clean solution is obtained, in which no phase separation, precipitation or gel formation is detected. The hydrolytic stability of the PPQ films was evaluated as follows: the PPQ film sample (80 mm ×10 mm × 0.05 mm) was immersed or boiled in deionized water for 24 h. Then, the samples were dried with blotter and then evaluated by resistivity measurements.

Synthesis of 9,9-Bis[(4-benzilyloxy)phenyl]fluorene (FLTK)

A mixture of 53.60 g (0.21 mol) of 4-nitrobenzil, 35.04 g (0.10 mol) of 9,9-bis(4-hydroxyphenyl)fluorene and 240 mL of anhydrous DMSO were added to a 500-mL three-necked flask equipped with a mechanical stirrer, a nitrogen inlet and a condenser. The reaction mixture was then heated to 60°C, and 69.11 g (0.50 mol) of anhydrous K_2CO_3 was added. The reaction was maintained for 20 h under nitrogen. Upon confirmation of the completion of the reaction by thin-layer chromatography, the solution was cooled to room temperature and then poured into a mixed solvent containing 2400 mL of 1 mol/L HCl and 600 mL of chloroform. The organic phase was collected and washed thoroughly with deionized water. Then, the chloroform solution was dried with $MgSO_4$. After distilling off the chloroform, a tan solid was obtained. The solid was purified by recrystallizations from acetic acid. The purified tetraketone FLTK was obtained as a pale yellow powder (41.42 g, yield: 54%).

Melting point: 212.8°C (DSC peak temperature). FT-IR (KBr, cm^{-1}): 1674, 1591, 1498, 1246, 1165 and 883. ^{1}H-NMR ($CDCl_3$): 6.94–6.96 (d, 4H), 7.01–7.03 (d, 4H), 7.24–7.26 (d, 4H), 7.31–7.34 (t, 2H), 7.40–7.44 (t, 4H), 7.50–7.54 (t, 4H), 7.65–7.69 (t, 2H), 7.80–7.82 (d, 2H), and 7.93–7.98 (m, 8H). ^{13}C-NMR ($CDCl_3$): 117.7, 120.2, 120.5, 126.1, 127.7, 127.9, 128.1, 129.1, 129.9, 130.0, 132.4, 133.2, 134.9, 140.2, 142.6, 150.9, 153.9, 163.5, 193.1, and 194.7. MALDI-TOF: 789 (M^+ + 23, 100). Elemental analysis: calculated for $C_{53}H_{34}O_6$: C, 83.01%; H, 4.47%. Found: C, 82.98%; H, 4.52%.

Synthesis of PPQs

Various PPQs were prepared by the reaction of FLTK and tetraamines in *m*-cresol. A typical synthetic route is as follows. To a 250 mL three-necked flask equipped with a mechanical stirrer, a condensator and a nitrogen inlet were added 3,3′,4,4′-tetraaminobiphenyl (4.2854 g, 0.02 mol) and anhydrous *m*-cresol (50 g) under nitrogen atmosphere. After stirring at room temperature for 10 min, a brown tetraamine solution was obtained. Then, FLTK (15.3370 g, 0.02 mol) was added in one batch and an additional volume of *m*-cresol (28 g) was added to wash the residual FLTK, and at the same time to adjust the solid content of the reaction system to be 20 wt%. The mixture was stirred at room temperature for 24 h to yield a viscous brown solution. Then, the solution was heated to 120°C and maintained for another 4 h. The obtained viscous solution was cooled to room temperature and slowly poured into an excess of methanol (500 mL) to yield a silky resin, yellow in color. The resin was immersed into methanol for 24 h, then collected and dried at 80°C in vacuum overnight to afford PPQ-1 resin. Yield: 18.64 g (95%).

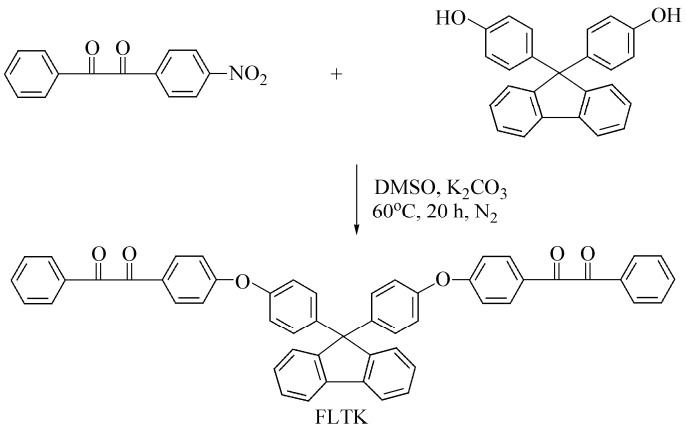
The well-dried silky PPQ-1 resin was dissolved in NMP at room temperature with a solid content of 15 wt%. The obtained PPQ solution was filtered through a 0.45 μm Teflon syringe filter to remove any contaminates that might affect the quality of the film. Then, the solution was cast onto a clean glass and PPQ-1 film was obtained by thermally baking the solution with the following heating procedure: 80°C/2 h, 150°C/1 h, 200°C/1 h, and 250°C/1 h.

The other PPQ resins and films, including PPQ-2, PPQ-3 and PPQ-4 were prepared according to a similar procedure as mentioned above.

RESULTS AND DISCUSSION

Monomer Synthesis

The new tetraketone compound FLTK was prepared through a nucleophilic substituent reaction of 4-nitrobenzil and 9,9′-bis(4-hydroxyphenyl)fluorene, as shown in Scheme 1. After recrystallization FLTK was obtained as a yellow solid with high purity for further polymerization.



Scheme 1 Synthesis of tetraketone monomer FLTK

The chemical structure of FLTK was identified by FT-IR, ^{1}H-NMR and ^{13}C-NMR. In the FT-IR spectrum (Fig. 1), the intensive absorption bands at 1674 cm^{-1} due to vibrations of α-dicarbonyl groups were obviously observed.

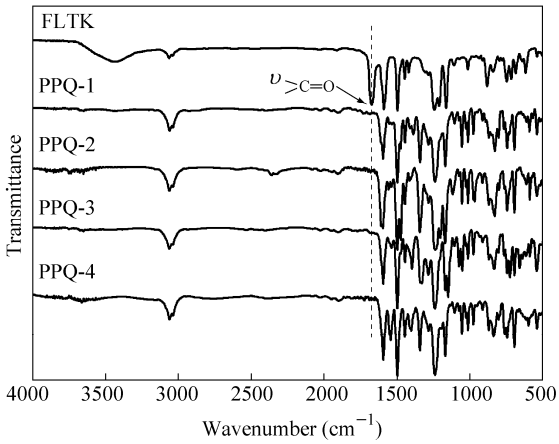
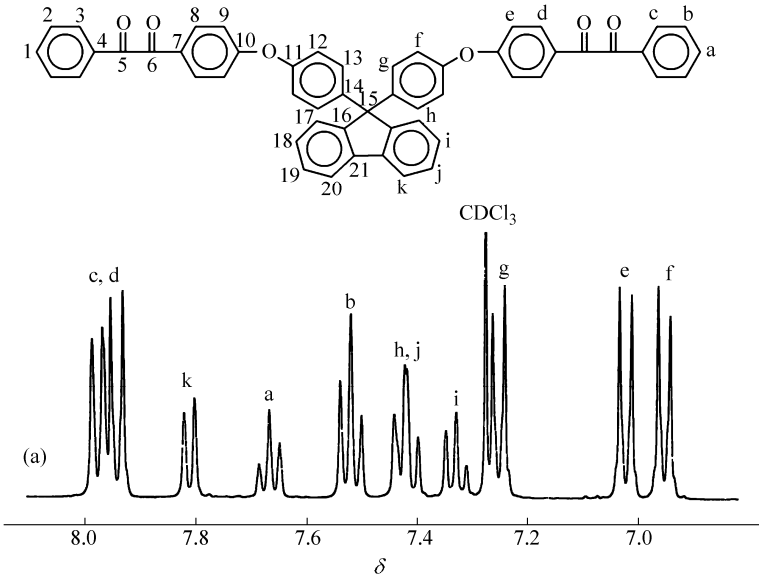


Fig. 1 FT-IR spectra of FLTK and PPQs

In the ^{1}H-NMR spectrum (Fig. 2a with inset showing molecular structure and detailed peak assignments), protons *ortho* to the electron-withdrawing α-dicarbonyl moiety (H_c and H_d) appeared around δ = 8.0, while protons *ortho* to the electron-donating ether linkage (H_e and H_f) appeared around δ = 7.0. This assignment well matched the proposed structure of the monomer. The structure of FLTK was verified further by its ^{13}C-NMR spectrum (Fig. 2b). As depicted in Fig. 2(b), 21 signals are clearly revealed due to the structure symmetry; among these, 11 carbons induce signals in the DEPT-135 measurements due to the existence of the attached protons. As anticipated, the tetraketone shows two signals (δ = 193.1 for C_6 and δ = 194.7 for C_5) at the lowest field in the spectrum due to nonequivalent carbonyls. This result is also consistent with the proposed structure.

Further characterization of FLTK by elemental analysis confirmed that the elemental components of the compound agreed well with the theoretical values. Thus, all the measurement results supported the successful synthesis of the high-purity monomer.



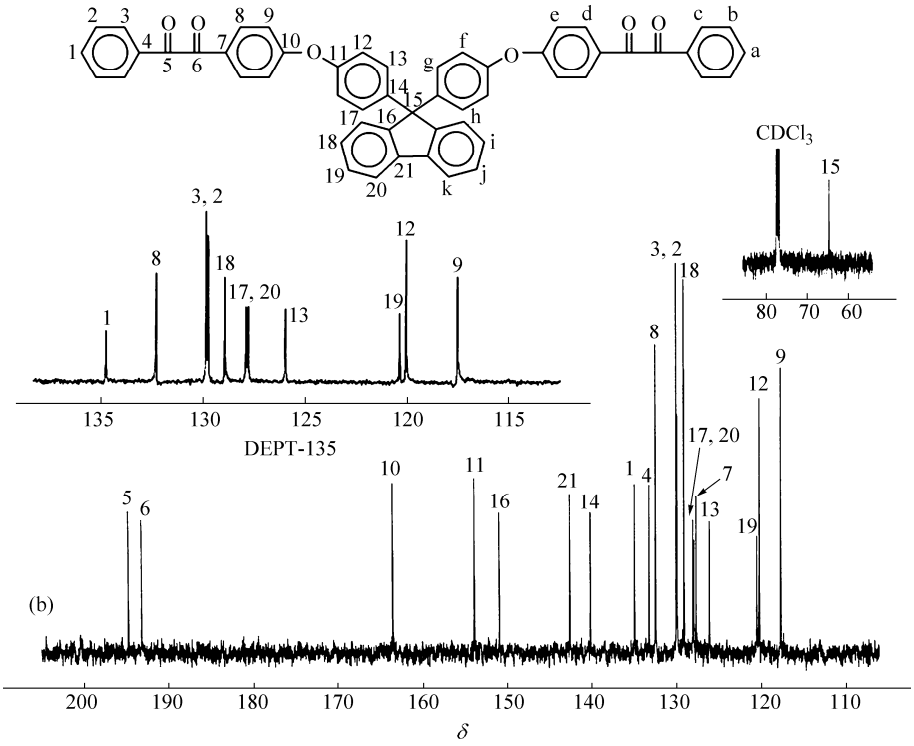
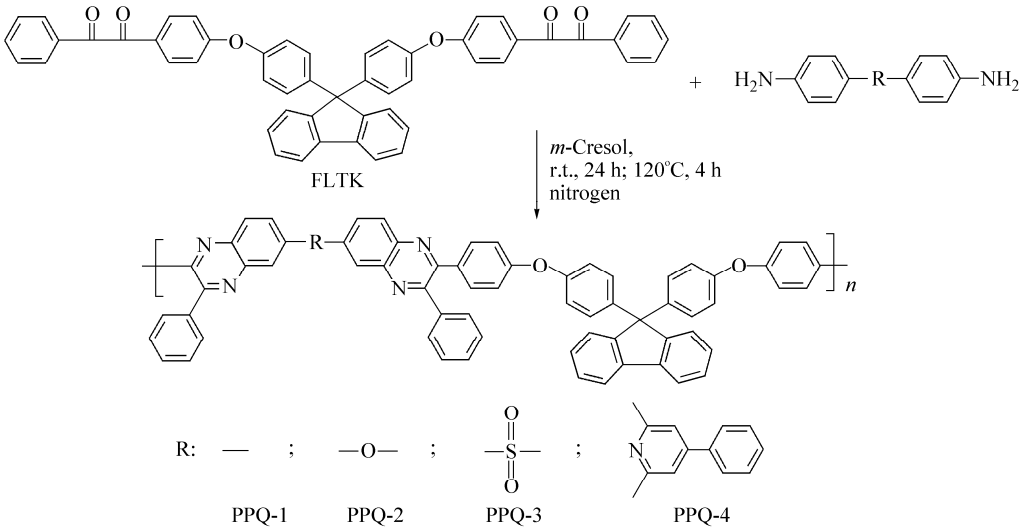


Fig. 2 NMR spectra of FLTK: (a) ^{1}H-NMR and (b) ^{13}C-NMR (DEPT-135 was embedded)

Polyphenylquinoxaline Synthesis

FLTK was polymerized with several tetraamines in *m*-cresol to afford PPQs (Scheme 2). The polymerizations were initially carried out at ambient temperature for 24 h. The obtained solutions were then heated at 120°C for another 4 h to complete the polymerizations. The PPQ products, which remained in solution, were isolated by precipitation in excess of methanol. IR spectra prove the formation of the target PPQs. A shown in Fig. 1, the characteristic absorption peak at 1674 cm^{-1} attributed to the carbonyl groups in FLTK disappeared in the spectra



Scheme 2 Synthesis of PPQs (PPQ-1–PPQ-4)

of PPQs. Instead, the characteristic absorption of －C＝N bonds in the quinoxaline ring were all observed at *ca*. 1596 cm^{-1} [29], confirming the successful transformation from the monomer to PPQs.

The structure of the PPQs was elucidated further by ^{1}H-NMR, as illustrated by the spectrum of PPQ-2 shown in Fig. 3. As expected, the protons in the cyclic quinoxaline rings (H_b and H_c) resonate at the lowest field in the spectrum. Contrarily, those *ortho* to the electron-donating ether linkage in the tetraketone moiety (H_e and H_f) exhibit absorption at the highest field in the spectrum.

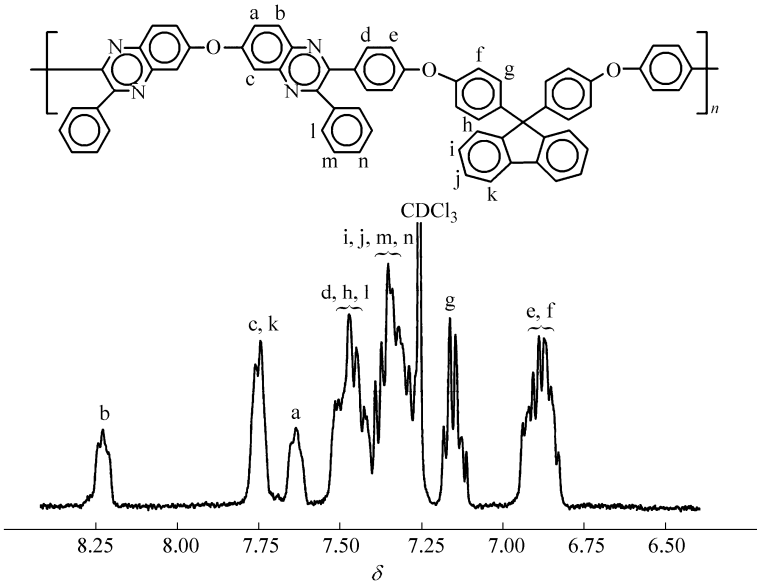


Fig. 3 ^{1}H-NMR spectrum of PPQ-2 (300MHz, $CDCl_3$)

The PPQs had inherent viscosities in the range of 0.68 dL/g to 0.84 dL/g in NMP at 30°C (Table 1). Flexible and tough PPQ films were cast from their NMP solutions. The tensile properties of the PPQ films are summarized in Table 2. They had tensile strength of 62–92 MPa, elongation at break of 4.4%–6.5% and tensile modulus of 2.3–2.8 GPa.

Table 1. Inherent viscosities and solubility of PPQs[a]

PPQ	$[\eta]_{inh}$ (dL/g)	Solvent						
		NMP	DMAc	*m*-Cresol	DMSO	THF	$CHCl_3$	Xylene
PPQ-1	0.84	++	+	++	+	+	++	–
PPQ-2	0.77	++	+	++	+	+	++	–
PPQ-3	0.68	++	++	++	+	++	++	–
PPQ-4	0.73	++	+	++	+	–	++	–

[a] $[\eta]_{inh}$: inherent viscosities measured with a PPQ resin at a concentration of 0.5 g/dL in NMP at 30°C;
++: wholly soluble at room temperature; +: partially soluble; –: insoluble

Table 2. Thermal and tensile properties of PPQ films [a]

PPQ	T_g (°C)	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	R_{w750} (%)	T_s (MPa)	E_b (%)	T_M (GPa)
PPQ-1	300	559	579	70	92	5.4	2.7
PPQ-2	281	554	566	66	85	6.5	2.4
PPQ-3	295	507	535	63	70	5.2	2.3
PPQ-4	308	558	573	72	62	4.4	2.8

[a] T_g: glass transition temperature; $T_{5\%}$, $T_{10\%}$: temperatures at 5% and 10% weight loss, respectively;
R_{w750}: residual weight ratio at 750°C in nitrogen; T_s: tensile strength; E_b: elongation at break; T_M: tensile modulus

The optical properties of the PPQ films were evaluated by UV-Vis spectra shown in Fig. 4. It is observed from Fig. 4 and the optical data listed in Table 3 that the present films possess acceptable optical transparency in the visible light region (450–800 nm). Apparently, the loose packing of PPQ chains due to the bulky fluorene units is beneficial for the penetration of visible lights. The transmittance values of the PPQs are all higher than 75% at 450 nm wavelength except PPQ-1. The more conjugated structures in PPQ-1 due to the rigid biphenyl moiety almost completely absorb the light in the wavelength region lower than 450 nm. Thus, PPQ-1 film is brownish in appearance while PPQ-3 and PPQ-4 are pale-yellow at the thickness of 10 μm.

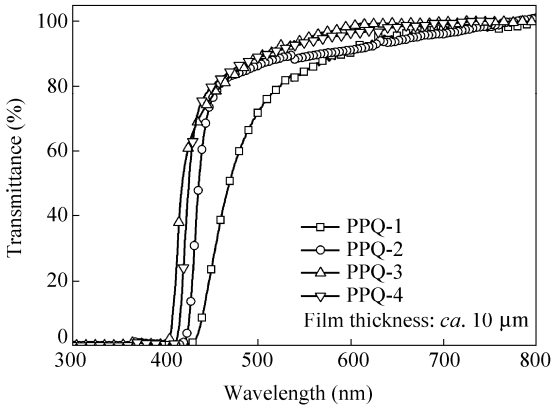


Fig. 4 UV-Vis spectra of PPQ films

Solubility

The solubility behavior of the PPQs in various solvents is summarized in Table 1. All of the polymers exhibited good solubility in *m*-cresol and chloroform. In addition, they were also soluble in polar aprotic solvent such as NMP. PPQ-3 derived from FLTK and sulfone-bridged tetraamine was even soluble in DMAc and THF. PPQ-4 containing rigid pyridine unit revealed the inferior solubility in the tested solvents due to the highly conjugated molecular structure in the tetraamine moiety. The good solubility of the present PPQs is mainly attributed to the relatively loose packing of the molecular chains resulting from the synergic effects of bulky fluorene units and flexible ether linkages in the polymers. The loose packing of polymer chains in the present PPQs could further be proven by the wide angel X-ray diffraction measurements, in which no crystallinity was observed for all of the polymers.

Thermal Properties

All the polymers were subjected to differential scanning calorimetry (DSC) and thermogravimetry analysis (TGA). Generally speaking, for the ether-bridged amorphous polymers such as polyetherimide, there is a considerable decrease in the rigidity and lowering of energy of internal rotation of polymer chains due to the presence of the flexible ether units, which usually reduces the T_g values of the polymers. This decrease could usually be recuperated by incorporation of bulky substituents in the 2- and 2′-positions of the diphenyl ether linkages in the polymers[30, 31]. The rotational flexibility along the ether linkage is expected to be decreased due to the steric effects of these substituents. In our previous work, we tried to increase the T_g values of ether-PPQs by introduction of *ortho*-substituted methyl groups[24]. Although this attempt was successfully achieved, the thermal stability of the obtained PPQs was somewhat sacrificed.

In the present study, clear glass transitions (T_g) were observed in the range of 281–308°C for all the PPQs when their DSC scans and rescans were run from room temperature to 400°C (Fig. 5). Obviously, the present ether-PPQs maintained a high level resistance to the elevated temperatures. It is noteworthy that the PPQ-4 exhibited a highest T_g value of 308°C, which is attributed to the rigid phenyl-attached pyridine unit in the polymer.

TGA plots (Fig. 6) showed that the current ether-PPQs were thermally stable. The decomposition of PPQs

was observed above 500°C in nitrogen for all polymers. PPQ-1 exhibited a $T_{5\%}$ value of 559°C. This value is comparable to those of PPQ-4 (558°C) and PPQ-2 (554°C); however, much higher than that of PPQ-3 (507°C). Actually, the thermally unstable nature of sulfone-bridged polymers has been widely noticed in the literature[32]. In addition, the residual weight ratios higher than 60% at 750°C further revealed the thermal stability of the present ether-PPQs. This confirms that our molecular design by incorporation of fluorene moiety for increasing the T_gs of ether-PPQs while maintaining their thermal stability is successful.

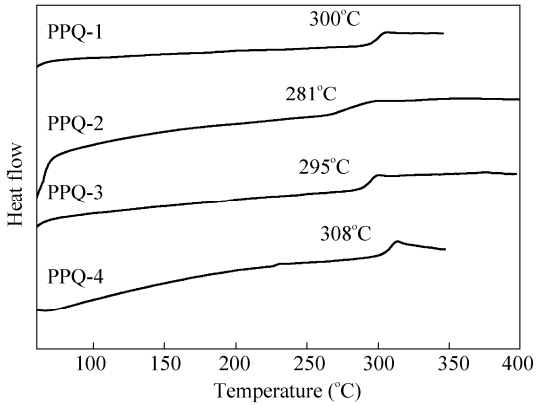


Fig. 5 DSC curves of PPQs (in nitrogen, 10 K/min)

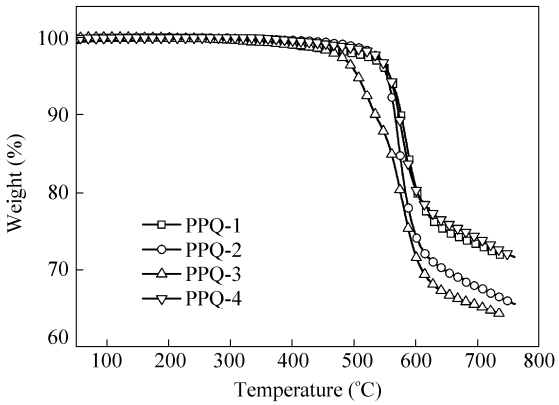


Fig. 6 TGA curves of PPQs (in nitrogen, 20 K/min)

Hydrolytic Resistance and Electrical Properties

One of the most attractive features for PPQs is their superior hydrolytic resistance as compared with the other high-temperature polymers such as polyimide and polybenzimidazole[15]. In order to investigate the hydrolytic stability of the PPQs, in the present study, the surface resistivity (ρ_s) and volume resistivity (ρ_v) of the polymers were utilized as the criteria. As we know, the resistivity of a dielectric can be influenced drastically by water. When the dielectric absorbs water or its structure was hydrolyzed by water, the resistivity of the material will deteriorate[33].

The electrical resistivity of PPQ-1 and PPQ-2 is tabulated in Table 3 and the data are compared in Fig. 7. It can be clearly seen that both of the resistivity values of the PPQs decreased after water treatment. For PPQ-1, the ρ_s value maintained 85.8% (determined by the ratio of ρ_{s2} to ρ_{s1}) and 51.7% (the ratio of ρ_{s3} to ρ_{s1}) of its original value after immersion or boiling in water for 24 h, respectively. With respect to the ρ_v value for PPQ-1, the retention data are 91.7% ($\rho_{v2}/\rho_{v1} \times 100\%$) and 68.7% ($\rho_{v3}/\rho_{v1} \times 100\%$), respectively. Similar trend was also observed for PPQ-2. Obviously, the PPQs exhibited good hydrolytic stability, which can be mainly attributed to the relatively low contents of water-sensitive polar groups in their structures.

Table 3. Optical and electrical properties of the PPQ films

Sample	λ [a] (nm)	T_{450} [a] (%)	$\rho_s \times 10^{-15}$ (Ω) [b]			$\rho_v \times 10^{-15}$ (Ω·cm) [c]		
			ρ_{s1}	ρ_{s2}	ρ_{s3}	ρ_{v1}	ρ_{v2}	ρ_{v3}
PPQ-1	430	24	12.0	10.3	6.2	81.7	74.9	56.1
PPQ-2	420	75	6.9	6.2	4.2	8.8	7.4	5.0
PPQ-3	410	76	– [d]	–	–	–	–	–
PPQ-4	403	80	–	–	–	–	–	–

[a] λ: cutoff wavelength; T_{450}: transmittance at 450 nm;

[b] ρ_s: surface resistivity; ρ_{s1}: ρ_s at 25°C; ρ_{s2}: ρ_s after immersion in water for 24 h; ρ_{s3}: ρ_s after boiling in water for 24 h;

[c] ρ_v: volume resistivity; ρ_{v1}: ρ_v at 25°C; ρ_{v2}: ρ_v after immersion in water for 24 h; ρ_{v3}: ρ_v after boiling in water for 24 h;

[d] Not measured

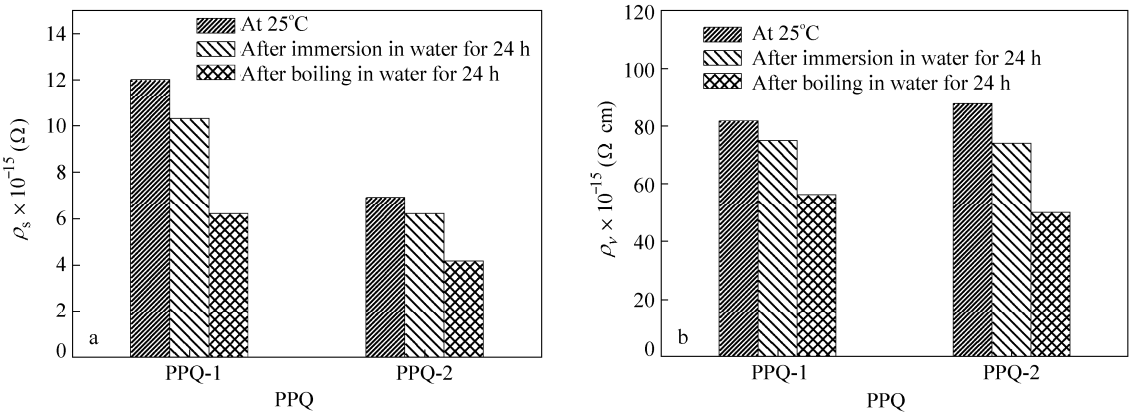


Fig. 7 Surface resistivity ρ_s (a) and volume resistivity ρ_v (b) of PPQs

CONCLUSIONS

A series of fluorene-bridged PPQs have been prepared from 9,9-bis[(4-benzilyloxy)phenyl]fluorene (FLTK) and aromatic tetraamines by a high temperature polycondensation procedure. All the PPQs are soluble in a variety of solvents and can be cast into flexible and tough films from their NMP solution. The films show T_g values higher than 280°C and $T_{5\%}$ data higher than 500°C. This result confirms that our molecular design aiming at increasing the T_g of ether-PPQs while maintaining their thermal stability is successful. In addition, the PPQ films exhibit good hydrolysis resistance, as evidenced by the high retention of surface and volume resistivity before and after hydrolysis in water. These characteristics make the present PPQs potential candidates for a variety of applications in electrical insulation, microelectronics and membrane technologies.

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