Synthesis and Characterization of Soluble Poly(ether imide)s Containing Fluorenyl Cardo Groups

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ABSTRACT: Two series of poly(ether imide)s (PEIs) containing fluorenyl cardo groups in the main chains were synthesized, which are derived from the polycondensation of 9,9′-bis(4-aminophenoxyphenyl)fluorene (BAOFL) or 9,9′-bis(3-trifluoromethyl,4-aminophenoxyphenyl)fluorene (6F-BAOFL) with four kinds of dianhydrides (3,3′,4,4′-biphenyl-tetracarboxylic dianhydride, 4,4′-oxydiphthalicanhydride, 3,3′,4,4′-benzophenone tetracarboxylic dianhydride, and bisphenol-A dianhydride), respectively. The PEI films and PEI powder were prepared by thermal and chemical imidization, respectively. The PEIs were characterized by FTIR, ^{1}H-NMR, differential scanning calorimetry, thermogravi-metric analysis, and UV–vis were performed on inherent viscosity, solubility, and tensile tests. The effects of fluorenyl cardo groups and ether linkages on the solubility, tensile properties, thermal stability, and optical properties were investigated in detail. It was found that the PEIs had good solubility in common organic solvents and good optical transparency in visible light region. In addition, the PEI films exhibited excellent tensile and thermal properties. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 3987–3993, 2009

Key words: poly(ether imide); fluorene; solubility; tensile properties; thermal stability; optical transparency

INTRODUCTION

Aromatic polyimides possess excellent thermal, mechanical, and electrical insulating properties, as well as chemical resistance, so they are widely used as electrical materials, adhesives, advanced composites, and high-temperature foams.[1–4] Generally, they are insoluble and infusible in their fully imidized form, leading to poor processability, which impose limitations to their application fields. To solve these problems, much research effort has been focused on the synthesis of soluble and melt processable polyimides without deteriorating their excellent properties.[5–14] Typical approaches are structural modification of polymer backbones. These have been achieved by incorporating flexible groups, such as ether link and sulfone, between aromatic rings. Also, asymmetrical, noncoplanar and kinked substituents have been introduced into polyimide backbones but at the expense of thermo-oxidative stability of the materials.

Most studies have shown that incorporating bulky lateral substituents, such as biphenyl-fluorene groups, into the polymer backbones afford aromatic polyimides high solubility, good thermal stability, high transparency, and high refraction index.[15–18]

Moreover, fluorene-based polyimides possess low dielectric constant, because the bulky fluorene groups inhibit the packing of chains and increase the free volume between chains. Therefore, the fluorene-based polyimides are widely used in fields of low dielectric constant material, gas separation membrane, proton exchange membrane of fuel cell, optoelectronic device, etc.[19–25]

By introducing fluorenyl cardo groups, the noncoplanar twisted diphenyl and the steric hindrance of the bulky substituents restrict the segmental motion, so the rigidity of polymer chains are preserved. However, fluorene-based polyimides are very brittle. We have known that introducing flexible groups such as ether links into main chains can make polyimides more flexible. Recent studies demonstrate that the incorporation of both fluorene and ether linkages into the molecular backbones result in polymers with improved solubility, thermal and mechanical properties.[17,26,27] The diamines containing both fluorene and ether linkages have been successfully synthesized in the few years.[17,26,27]

In light of these observations, we aim to synthesize two series of poly(ether imide)s (PEIs), which contain both rigid fluorenyl cardo groups and flexible ether linkages in polymer main chains, based on two new diamine monomers. The two diamines are 9,9′-bis(4-aminophenoxyphenyl)fluorene (BAOFL) and 9,9′-bis(3-trifluoromethyl, 4-aminophenoxyphenyl)fluorene (6F-BAOFL). BAOFL and 6F-BAOFL

TABLE I
PEIs Synthesized in the Experiment

System no.	Components	Dianhydrides			
		BPDA	ODPA	BTDA	BPADA
1	BAOFL/dianhydrides	1a	1b	1c	1d
2	6F-BAOFL/dianhydrides	2a	2b	2c	2d

were subjected to polymerization with four kinds of aromatic dianhydrides [3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA), 4,4′-oxydiphthalicanhydride (ODPA), 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTDA), and bisphenol-A dianhydride (BPADA)], respectively. The PEI films and PEI powder were prepared by thermal and chemical imidization, respectively. The influence of molecular structure of monomers on the inherent viscosity, solubility, tensile properties, thermal stability, and optical properties of the synthesized PEIs were discussed in detail. So far, the synthesis and properties of PEIs derived from different kinds of dianhydride and diamine BAOFL or 6F-BAOFL, especially for 6F-BAOFL, have not been reported.

EXPERIMENTAL

Materials

The diamines BAOFL and 6F-BAOFL were prepared as described in the literature,[17,26,27] which were dried under vacuum at 80°C for 6 h before use.

The dianhydrides BPDA, ODPA, BTDA, and BPADA) were dried under vacuum at 150°C for 8 h before use. These dianhydrides were purchased from Shanghai Research Institute of Synthetic Resins.

N-Methyl-2-pyrrolidone (NMP) was purified by distillation under reduced pressure over calcium hydride. It was purchased from Beijing Chemical Reagents Company.

Preparation of PEIs

The monomer compositions of PEIs are summarized in Table I.

The PEIs were synthesized in two forms, i.e., films and powder via two-step method involving formation of poly(amide acid) (PAA) solution. A typical polymerization procedure of PAA solution was as follows. In a 100 mL three-necked flask, after complete dissolution of diamine in NMP solution, the stoichiometric amount of dianhydride was added. The reaction mixture was stirred at room temperature for 24 h to afford the soluble PAA solution.

PEI film was produced by imidization from PAA solution as precursor. The PAA solution (20 wt % in NMP) was coated on a clean glass plate, followed by

far-infrared imidization in a far-infrared radiation oven with six-stage heating procedure (80°C for 2 h and 150, 200, 250, 300, and 350°C for 1 h).

PEI in powder form was obtained via chemical imidization, which was performed by addition of acetic anhydride and pyridine into PAA solution, followed by stirring the mixture for 12 h at room temperature. Then, the homogeneous solution was added slowly into methanol and the fibrous solid was collected by filtration. The filtered solid was washed thoroughly with methanol and again filtered. Finally, the solid was dried under vacuum at 120°C for 8 h before use.

Measurements

Infrared spectra were recorded on a Nexus-470 FTIR spectrometer. ^{1}H-NMR spectra were obtained at 400 MHz using a Bruker AVANCE III-400 NMR spectrometer using deuterated dimethyl sulfoxide (DMSO-d_6) as the solvent, and chemical shifts were reported in ppm units with tetramethylsilane as internal standard. The inherent viscosity of PEI was measured at polymer concentration of 0.5 g/dL in NMP solution at room temperature using an Ubbelhode viscometer. The solubility of PEIs in different organic solvents were checked as follows. Three grams of fully dried PEI was mixed with 17 mL solvent, which was prepared to 15% (w/v) solid content solution. Then, it was kept in a dryer for 24 h to observe the phenomenon. If the solution was uniform and transparent, we considered that the PEI dissolved in the solvent. Otherwise, we believed that the PEI was partially soluble or insoluble in the solvent. Tensile properties were determined from stress–strain curves measured with a INSTRON-5565 mechanical testing machine at a tensile speed of 5 mm/min. Measurements were performed at room temperature with film specimens of 10 mm width, 120 mm length, and 40–50 μm thickness. The tensile modulus was tested by infrared video extensometer. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed with Seiko DSC 6300 instrument and TG/DTA 6300 instrument, respectively, in nitrogen atmosphere at a heating rate of 10°C/min. UV–vis absorption spectra were recorded on a Hitachi U-3210 UV–vis spectrophotometer.

RESULTS AND DISCUSSION

Synthesis and structure of PEIs

The chemical structure of PEIs were identified by FTIR spectra, which were shown in Figure 1. As shown in Figure 1(b), the characteristic absorption bands of imide rings at 1778 cm^{-1} (unsymmetric stretching vibration of C=O), 1720 cm^{-1} (symmetric stretching vibration of C=O), 1374 cm^{-1} (unsymmetric stretching vibration of C—N), and 744 cm^{-1} (deformation of imide ring) were very evident. Moreover, as shown in Figure 1(a), the absence of hydrogen bond (O—H) vibration bands at 3100–3500 cm^{-1} indicated the complete imidization of the PEIs. The absorption at 1509 cm^{-1} was assigned to the sketch vibration for p-substituted phenyl ring of BAOFL or 6F-BAOFL and the absorption at 1240 cm^{-1} was assigned to the stretch vibration for ether link contained in the main chain of PEI.

The synthetic route of PEI derived from BAOFL and BPDA is shown in Figure 2. The molecular structure of 6F-BAOFL and other dianhydrides are also shown in Figure 2.

The chemical structure of PEIs were also analyzed by ^{1}H-NMR spectra. The typical ^{1}H-NMR spectrum is shown in Figure 3. The resonances for the aromatic protons were well consistent with the supposed structure of the PEI. ^{1}H-NMR (400MHz, DMSO-d_6, ppm): 7.06–7.08 (d, 4H), 7.16–7.18 (m, 2H), 7.22–7.24 (m, 4H), 7.36–7.38 (m, 2H), 7.43–7.45 (m, 2H), 7.49–7.51 (d, 2H), 7.62–7.64 (m, 2H), 7.68, 7.70 (m, 4H), 7.90 (s, 2H), 7.95–7.97 (d, 2H), and 8.06–8.08 (d, 2H).

Solubility of PEIs

In the process of chemical imidization, the solution was homogeneous all the time, which indicated that the fully imidized PEI could dissolve in the solvent. The inherent viscosity of PAAs or PEIs and the solubility of PEIs in different organic solvents were checked at room temperature, and the results were summarized in Table II.

As shown in Table II, the PAAs possessed higher inherent viscosity in the range of 0.82–1.43 dL/g and the PEIs possessed inherent viscosity in the range of 0.69–1.16 dL/g, which showed the PEIs had larger molecular weight. The inherent viscosity of PEIs 2a-2d were lower than those of PEIs 1a-1d, which could be attributed to the introduction of bulky trifluoromethyl groups in the molecular chains of PEIs 2a-2d. The presence of trifluoromethyl groups damage the electronic conjugation in PEI molecular structure and inhibit the formation of charge transfer complex, which reduce the interchain interaction and enhance the flexibility of polymer, so the inherent viscosity is decreased.

PEIs synthesized from 6F-BAOFL and dianhydride (BPDA, ODPA, or BPADA) possessed the best solubility, which dissolved in each solvent used in the experiment. The excellent solubility of these PEIs could be attributed to two factors. First, the presence of trifluoromethyl groups enhance the solubility of polymer. Second, PEIs synthesized from 6F-BAOFL have bulky noncoplanar diphenylfluorene groups and flexible ether linkages in the main chains, which restrict the close packing of the polymer chains and thereby lessen the probability of interchain interaction, resulting in an easier solvation pathway and high solubility.

The solubility of PEIs 1c and 2c were the worst. PEI 1c did not dissolve in any solvent used in the experiment. PEI 2c only partially dissolved in tetrahydrofuran (THF) and 1,2-dichloroethane solvents. PEIs 1c and 2c were both synthesized from BTDA. The carbonyl group (C=O) contained in BTDA molecular structure can complex with the ether group (—O—) contained in diamine molecular structure,
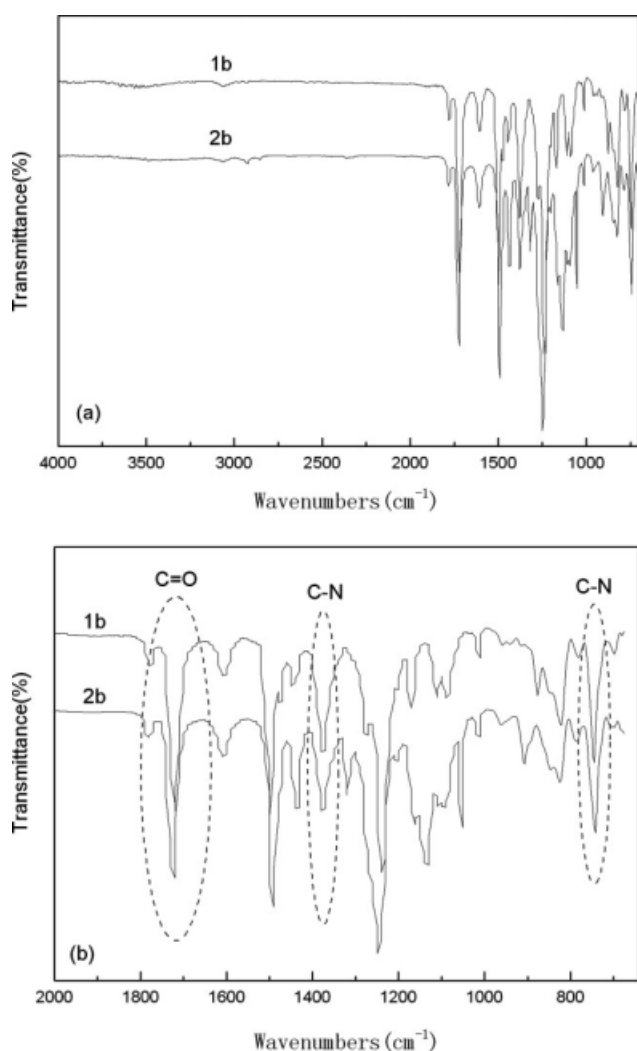

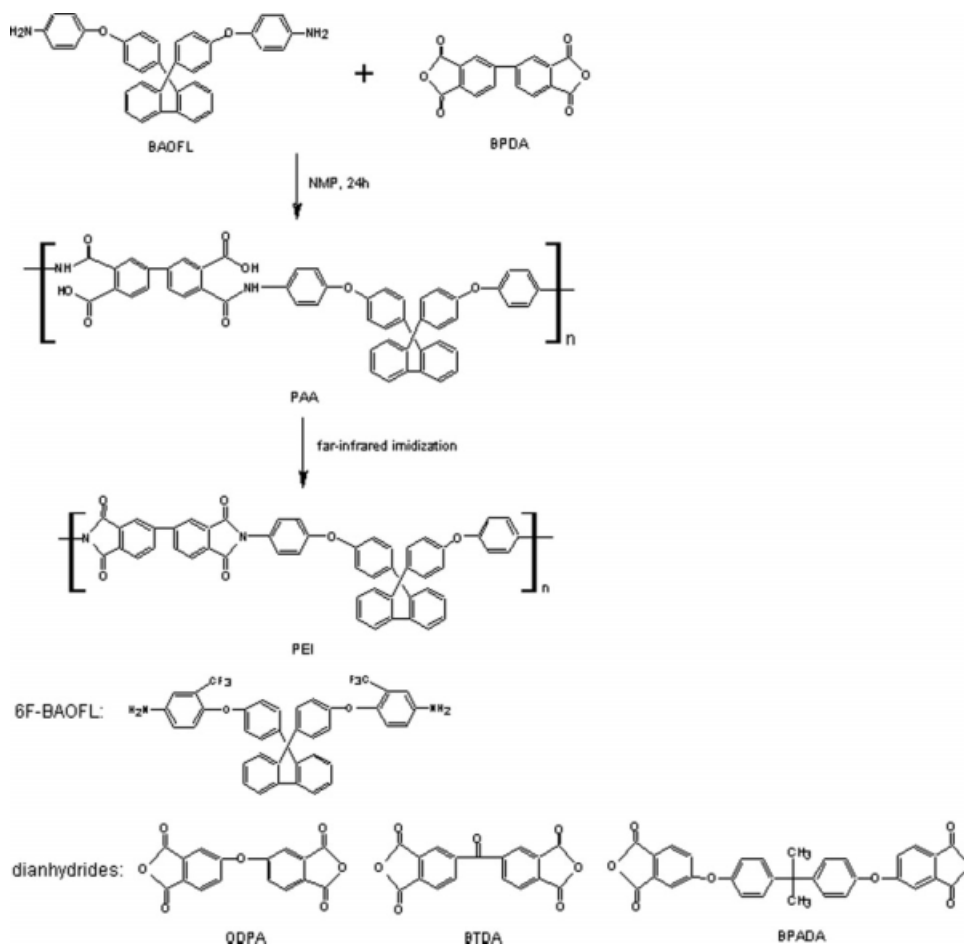**Figure 1** FTIR of PEI films.

Figure 2 Synthetic routes of PEIs.

which form the charge transfer complex as shown in Figure 4. So, the PEI chains consist of two alternating chemical units of different electronic nature: electron accepting diimide structural fragments and electron donating phenoxy components. Donor–acceptor interaction of these groups improve the interchain interaction and decrease the distances between chains, which inhibit the dissolution of polymer chains in organic solvents. PEIs 1a, 1b, and 1d exhibited good solubility in aprotic polar solvents, such as NMP, N,N-dimethylformamide (DMF), and N,N-dimethylacetamide (DMAc).

These amorphous PEIs possess good solubility in common organic solvents. Such excellent solubility of the PEIs will be attributed to the existence of both bulky diphenylfluorene substituents and flexible groups in polymer main chains, which bring high steric hindrance to decrease the interchain interaction and also provide an easier solvation pathway.

Tensile properties of PEIs

The PEI films were subjected to tensile tests, and the results were summarized in Table III.

The PEI films have tensile strength of 76.4–104.9 MPa, tensile modulus of 2.9–3.5 GPa, elongation-at-break of 8.9–15.6%, indicating that they had good tensile properties. As shown in Table III, the tensile properties of PEIs synthesized from 6F-BAOFL were worse than those synthesized from BAOFL, which might be due to the introduction of trifluoromethyl groups in 6F-BAOFL. The presence of bulky trifluoromethyl groups damage the electronic conjugation in PEI molecular structure and inhibit the formation
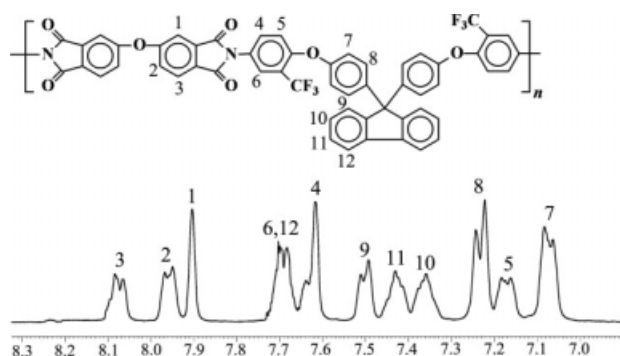

Figure 3 ^{1}H-NMR spectrum in the aromatic region of PEI 2b in DMSO-d_6.

TABLE II
Structural Analysis of PEIs at Room Temperature

PEIs	$[\eta]_{inh,PAA}^{a}$ (dL/g)	$[\eta]_{inh,PEI}^{b}$ (dL/g)	Solubility[c]						
			NMP	DMF	DMAc	m-cresol	THF	Toluene	1,2-Dichloro ethane
1a	1.43	1.16	++	++	++	+	−	−	−
1b	1.26	1.02	++	++	++	−	++	−	++
1c	1.18	0.97	−	−	−	−	−	−	−
1d	1.07	0.91	++	++	++	−	+	−	++
2a	1.15	0.96	++	++	++	+	++	+	++
2b	1.01	0.81	++	++	++	++	++	++	++
2c	0.92	0.74	−	−	−	−	+	−	+
2d	0.82	0.69	++	++	++	++	++	++	++

[a] $[\eta]_{inh,PAA}$, inherent viscosity measured with PAA solution.
[b] $[\eta]_{inh,PEI}$, inherent viscosity measured with PEI solution.
[c] ++, wholly soluble; +, partially soluble; −, not soluble.

of charge transfer complex, which reduce the interchain interaction, so the tensile properties are decreased. The dianhydrides of ODPA and BPADA have flexible linkages, whereas BPDA does not have any flexible groups. The flexible structural feature could increase the segmental motion, so the tensile strength and modulus of PEI films derived from ODPA or BPADA were lower than those of PEI films derived from BPDA. However, the elongation-at-break of PEI films derived from ODPA or BPADA were higher than those of PEI films derived from BPDA. The PEI films synthesized from BTDA had the highest tensile modulus. The carbonyl group (C=O) contained in BTDA molecular structure can complex with the ether group (—O—) contained in diamine molecular structure, which form the charge transfer complex. Donor–acceptor interaction of these groups improve the interchain interaction.

Thermal properties of PEIs

The thermal properties of fluorene-based PEIs were evaluated by DSC and TGA, respectively. The TGA curves are shown in Figure 5. Thermal properties of PEIs are summarized in Table IV.

From Table IV, we know that the introduction of rigid fluorene groups afford PEIs exhibiting high T_g values and excellent thermal stability even though the PEIs show high solubility. As for PEIs synthesized from BAOFL and different dianhydrides, the T_g values of PEIs were in the range of 256–321°C. As PEIs synthesized from 6F-BAOFL and different dianhydrides, the T_g values of PEIs were in the range of 245–303°C. The T_g values of PEI 2a–2d were lower than those of PEI 1a–1d, which might be due to the introduction of trifluoromethyl groups decreasing interchain interaction, thus leading to decreased T_g values.

As shown in Figure 5, all of the PEIs appeared similar in patterns of decomposition, without significant weight loss up to 500°C in nitrogen. The 5 and 10% weight loss temperatures were above 493 and 513°C, respectively. The residual weight of PEIs were all above 59% at 700°C. The excellent thermal stability could be attributed to the difficult moving of rigid polymer chains in high temperature. From Table IV, we know that the thermal stability of PEIs synthesized from 6F-BAOFL were better than those synthesized from BAOFL.
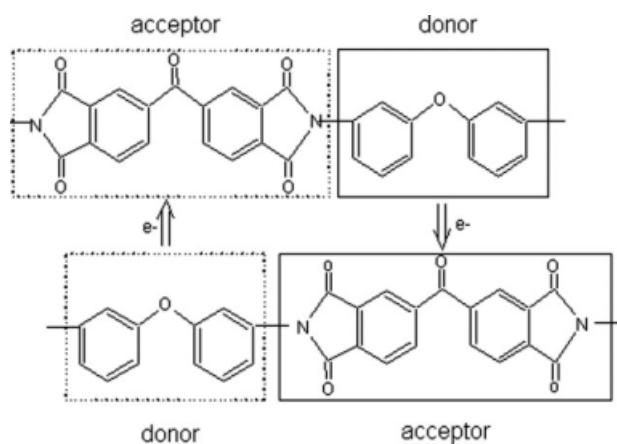

Figure 4 Model of charge transfer complex.

TABLE III
Tensile Properties of PEI Films

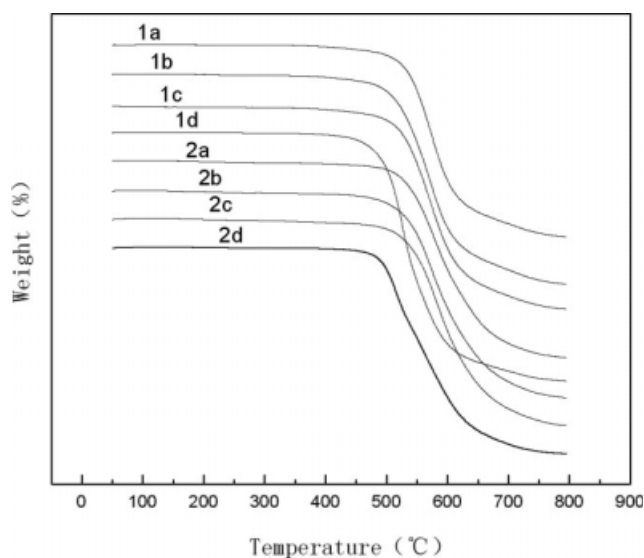| PEIs	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation-at-break (%)
1a	104.9	3.3	10.3
1b	90.2	3.3	15.6
1c	97.1	3.5	12.9
1d	82.0	3.1	14.2
2a	93.7	3.2	8.9
2b	84.1	3.0	13.9
2c	90.8	3.3	11.5
2d	76.4	2.9	12.6

Figure 5 TGA of PEIs.

Figure 6 UV–vis spectra of PIs.

UV–vis spectra of PEIs

The UV–vis spectra of PEIs and the reference PI derived from PMDA and 4,4′-ODA are shown in Figure 6.

From Figure 6, we know that the PEIs possess good optical transparency in visible light region. The cutoff wavelength of PEIs 1a and 2a were 378 and 359 nm, respectively, which meant that they were almost transparent at wavelength greater than 378 nm. The transmittance at 450 nm were 74.2 and 77.9%, respectively, whereas the transmittance at 450 nm of PI derived from PMDA and ODA was only 13.3%. The optical transparency of PEI 2a was better than that of PEI 1a, which could be due to the introduction of trifluoromethyl groups in PEI 2a. The electron-withdrawing trifluoromethyl groups effectively damage the electronic conjugation in PEI molecular chain and inhibit the formation of interchain charge transfer complex. Therefore, the absorption of
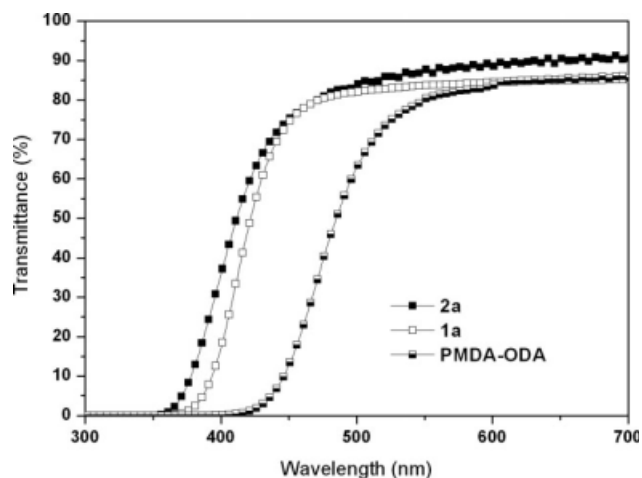
PEI containing trifluoromethyl groups in visible light region is decreased and the optical transparency is enhanced.

CONCLUSIONS

Two series of PEIs containing fluorenyl cardo groups in the main chains were successfully synthesized. Transparent, flexible PEI films were obtained by solution casting. The bulky and twisted noncoplanar structural feature conferred enhanced solubility of PEIs because of decrease in the degree of molecular packing while imparting significant increase in both T_g values and thermal stability by restricting segmental mobility. UV–vis spectra indicated that PEIs have good optical transparency in visible light region. In addition, the PEI films exhibited excellent tensile properties. Introducing trifluoromethyl groups in PEIs, the solubility, thermal stability, and optical transparency were enhanced, but the tensile properties, T_g values were reduced.

TABLE IV
Thermal Properties of PEIs

PEIs	T_g (°C)	$T_{5\%}$[a] (°C)	$T_{10\%}$[b] (°C)	Char yield[c] (%)
1a	321	536	557	69
1b	295	518	543	66
1c	312	523	548	67
1d	256	493	513	59
2a	303	541	566	69
2b	281	535	561	67
2c	289	542	568	68
2d	245	508	525	67

[a] 5% weight loss temperature in TGA at 10°C/min heating rate.
[b] 10% weight loss temperature in TGA at 10°C/min heating rate.
[c] Residual weight in TGA at 700°C under nitrogen atmosphere.

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