



Synthesis and properties of novel polyimides based on 10,10-bis[4-(4-aminophenoxy)phenyl]-9(10H)-anthrone

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Abstract

A new aromatic diamine bearing ether and pendant 9(10H)-anthrone groups, 10,10-bis[4-(4-aminophenoxy)phenyl]-9(10H)-anthrone was reacted with various aromatic dianhydrides to yield the corresponding cardo polyimides via the poly(amic acid) (PAA) precursors and thermal or chemical imidization. The PAAs were produced with moderate to high inherent viscosities of 0.91–1.53 dL/g. All the PAAs could be cast from DMAc solution and thermally converted into transparent, flexible and tough polyimide films with tensile strength of 79.6–115.2 MPa, tensile modulus of 1.97–2.48 GPa, and elongation at break of 10.8–21.7%. These polyimides were predominantly amorphous, and displayed excellent thermal stability with glass-transition temperature of 290–359 °C, 10% weight loss temperature of 522–566 °C, and the residue of 59–65% at 800 °C in nitrogen. Most of the polyimides obtained by chemical cyclodehydration procedure were found to be soluble in NMP, DMF and m-cresol at room temperature.

Keywords Cardo polyimides · 10,10-Bis[4-(4-aminophenoxy)phenyl]-9(10H)-anthrone · Thermal property · Solubility · Mechanical property

Introduction

Aromatic polyimides (PIs) have been of great interest for a number of applications in microelectronics, automobile, aerospace and other fields as a result of their good thermal stability and chemical resistance, excellent mechanical and electrical properties [1–4]. However, their insolubility in common organic solvents and their high glass and softening temperatures make them difficult to process and fabricate. In order to overcome these shortcomings and meet the demands of high technology, the development of heat-resistant, soluble, easy to process and high-strength polyimides has attracted great interest of researchers. It is well known that incorporation of flexible linkage such as ether, thioether, sulfone, methylene and isopropylidene groups into polymer backbone is a common

approach for improving the solubility and processability of the polyimides [5–15]. But, at the same time, these flexible linkages tend to lower the glass transition temperatures. It has been demonstrated that the presence of cyclic side groups (usually named as cardo groups) such as fluorine [16, 17], phthalide [18, 19], cyclododecane [20], or cyclohexane [21, 22] in the repeat unit of polymer resulted in enhanced solubility and high thermal properties of the polyimides. 9(10H)-Anthrone is a kind of rigid, large volume molecule, which can be used to construct cardo-type diamine or dianhydride monomers. The 9(10H)-anthrone group was once incorporated into the main chains of several polymers such as poly(1,3,4-oxadiazole)s and polyarylates derived from 10,10-bis(4-carboxyphenyl)-9(10H)-anthrone, as well as polyimides and polyamides based on 10,10-bis(4-aminophenyl)-9(10H)-anthrone to improve their properties [23]. Obviously, the introduction of cardo 9(10H)-anthrone groups into the polymer backbone would be a potential modification to the structure of rigid polymers. When combined with the polyimide framework, 9(10H)-anthrone units may block the chain stacking, resulting in the free volume of molecular scale entering the polymer film, thus promoting its application in photoelectron and gas separation. Moreover, insertion of both ether and 9(10H)-anthrone units simultaneously into the polymer backbone may endow the

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polyimides with a combination of desired properties. However, it is rarely reported that 9(10*H*)-anthrone group and ether bond are fused into aromatic diamine monomers for the synthesis of new polyimides. Owing to the unique structural feature of 9(10*H*)-anthrone, synthesizing and characterizing new poly(ether imide)s bearing 9(10*H*)-anthrone moieties in the polymer backbone are interesting enough to be investigated further. Based on our research of xanthene-containing cardo polyimides [24, 25], and a continuation of studies toward the development of new aromatic polyimides, we report herein the synthesis of a series of 9(10*H*)-anthrone-tape cardo aromatic poly(ether imide)s, from a new diamine, 10,10-bis[4-(4-aminophenoxy)phenyl]-9(10*H*)-anthrone and commercial aromatic dianhydrides. It was expected that incorporation of 9(10*H*)-anthrone moieties together with the ether linkage into the polymer backbone could improve the solubility, decrease the color intensity, and preserve thermal stability.

Experimental

Materials

All chemicals such as 9(10*H*)-anthrone, phenol, thionyl chloride, 4-chloronitrobenzene, hydrazine monohydrate, and 10% palladium on activated carbon (Pd/C) were obtained commercially, and were used as received unless otherwise specified. The following reagents and solvents have been treated as follows prior to use. Aromatic dianhydrides such as pyromellitic dianhydride (**PMDA**, **4a**), 3,3',4,4'-biphenyltetracarboxylic dianhydride (**BPDA**, **4b**), 4,4'-oxydiphthalic anhydride (**ODPA**, **4c**), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (**BTDA**, **4d**), 4,4'-sulfonyldiphthalic anhydride (**SDPA**, **4e**), and 4,4'-hexafluoroisopropylidenediphthalic anhydride (**6FDA**, **4f**) were recrystallized from acetic anhydride. Xylene was refluxed with sodium and distilled under reduced pressure. *N,N*-Dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc) and pyridine (Py) were purified by distillation under reduced pressure over calcium hydride. Potassium carbonate was dried in vacuo at 130 °C for 12 h.

Characterization

Fourier transform infrared (FTIR) spectra of intermediates, monomer and polyimides were recorded on a Perkin-Elmer SP One FT-IR spectrometer. ¹H and ¹³C NMR spectra were obtained on a Bruker Avance 400 MHz spectrometer with deuterated chloroform or dimethyl sulfoxide as the solvents and tetramethylsilane (TMS) as an internal standard. Elemental analyses were performed on Euro Vector EA3000 Elemental Analyses. Differential scanning calorimetry (DSC) was carried out on a Perkin-Elmer DSC-7 system at a heating rate of 20 °C/min in flowing nitrogen (40 cm³/min). Glass-

transition temperatures (*T*_gs) were read at the middle of the transition in the heat capacity and were taken from the second heating scan after the sample was cooled to room temperature. Thermogravimetric analysis (TGA) was conducted with a Perkin Elmer Pyris 1 TGA with approximately 5 mg of polymer samples at a heating rate of 10 °C/min under nitrogen atmosphere (30 mL/min). Inherent viscosities of PAAs and PIs were determined on 0.5 g/dL concentration of polymer in DMAc using an Ubbelohde capillary viscometer at 30 ± 0.1 °C. Molecular weights were determined by a gel permeation chromatography (GPC) with polystyrene calibration using a Waters 510 high performance liquid chromatography equipped with 5-μm phenogel columns (linear, 3 × 500 Å) arranged in series and a UV detector at 254 nm using tetrahydrofuran as eluent. The mechanical properties of the films were determined on a mechanical tester Instron 1122 instrument with a 5-kg load cell at a crosshead speed of 5 mm/min on strips (0.5 cm wide, 6 cm long, and ca. 0.05 mm thick) at 25 °C, and an average of at least four individual determinations was used. Wide angle X-ray diffraction (WAXD) data were collected on a Rigaku Geiger Flex D-Max III x-ray diffractometer with a Ni-filtered CuK_α source, operated at 40 kV and 15 mA at room temperature, and the samples were scanned from 5 to 80 ° at a scanning rate of 2 °/min.

Synthesis of intermediates and monomer

10,10-Bis(4-hydroxyphenyl)-9(10*H*)-anthrone (**1**, **BHPA**):

A mixture of 9(10*H*)-anthrone (9.7 g, 50 mmol) and sulfoxide chloride (30 mL) was refluxed for 6 h. After removing the excess of sulfoxide chloride under vacuum, phenol (18.8 g, 200 mmol) and xylene (30 mL) were added to the reaction mixture, which was heated to reflux with stirring for 8 h. After the reaction, excess phenol and toluene were removed from the reaction system by steam distillation. Then, the mixture was cooled to room temperature, and the crude product was obtained by filtration, washed with a small amount of dichloromethane, and recrystallized from acetone to give a light gray solid, **BHPA** (16.0 g, 85%); mp = 306–307 °C (determined by DSC) [23]. ¹H NMR (400 MHz, DMSO-*d*₆): δ = 9.44 (s, 2 H), 8.11 (d, *J* = 9.6 Hz, 2 H), 7.59 (t, *J* = 7.0 Hz, 2 H), 7.47 (t, *J* = 6.8 Hz, 2 H), 7.16 (d, *J* = 7.8 Hz, 2 H), 6.72 (d, *J* = 8.8 Hz, 4 H), 6.65 (d, *J* = 8.8 Hz, 4 H). FTIR (KBr): ν_{max} = 3064, 3034, 1664, 1600, 1506, 1445, 1234, 1176, 869, 760 cm⁻¹.

10,10-Bis[4-(4-nitrophenoxy)phenyl]-9(10*H*)-anthrone (**2**):

In a 250 mL round-bottomed, three-necked flask equipped with a condenser, magnetic stirrer bar and a nitrogen gas inlet tube, a mixture of **BHPA** (3.78 g, 10 mmol), K₂CO₃ (3.45 g, 10 mmol), 4-chloronitrobenzene (3.15 g, 20 mmol) in anhydrous DMF (60 mL) was heated and refluxed for 8 h. After the reaction, the reaction mixture was cooled to room temperature, and poured into 100 mL of methanol /water (1:1). The crude product was collected by filtration, washed

thoroughly with water, dried, and recrystallized from petroleum ether/dichloromethane to give a light-yellow needle crystals (**2**) (5.27 g, 85%); mp = 237–238 °C (determined by DSC). ^1H NMR (400 MHz, CDCl_3): δ = 8.32 (d, J = 7.6 Hz, 2 H), 8.20 (d, J = 8.6 Hz, 4 H), 7.57 (t, J = 7.4 Hz, 2 H), 7.50 (t, J = 7.4 Hz, 2 H), 7.19 (d, J = 8.0 Hz, 2 H), 7.07–7.02 (m, 8 H), 6.97 (d, J = 8.6 Hz, 4 H). ^{13}C NMR (100 MHz, CDCl_3): δ = 184.4, 162.7, 153.8, 148.7, 143.0, 133.4, 132.9, 132.4, 131.9, 130.3, 127.8, 127.7, 126.0, 119.8, 117.6, 57.4. Elem. Anal. Calcd. for $\text{C}_{38}\text{H}_{24}\text{N}_2\text{O}_7$: C 73.54%, H 3.90%, N 4.51%; found C 73.80%, H 3.98%, N 4.40%. FTIR (KBr): ν_{max} = 3079, 1657 (Ar–CO–Ar stretching), 1592, 1491, 1519 and 1339 (–NO₂ stretching), 1245 (Ar–O–Ar stretching), 1168 and 1111 (Ar–O–Ar stretching), 932, 882, 847, 739 cm^{-1} .

10,10-Bis[4-(4-aminophenoxy)phenyl]-9(10H)-anthrone (3, BAPA): A mixture of the dinitro compound (**2**) (9.30 g, 15 mmol), anhydrous ethanol (150 mL), and a catalytic amount of 10% Pd/C (0.1 g) was added to a 250 mL three-necked flask equipped with a dropping funnel and a reflux condenser. After heated to the refluxing temperature with stirring, hydrazine monohydrate (15 mL) was added dropwise in 1 h, the mixture was refluxed for additional 12 h. The mixture was then filtered to remove Pd/C. After cooling, the precipitated white solid was isolated by filtration and recrystallized from ethanol to afford white needle crystals **BAPA (3)** (7.40 g, 88%); mp = 250–251 °C (determined by DSC). ^1H NMR (400 MHz, CDCl_3): δ = 8.27 (d, J = 7.6 Hz, 2 H), 7.49 (t, J = 7.4 Hz, 2 H), 7.42 (t, J = 7.4 Hz, 2 H), 7.17 (d, J = 8.0 Hz, 2 H), 6.88–6.84 (m, 8 H), 6.74 (d, J = 9.2 Hz, 2 H), 6.65 (d, J = 7.6 Hz, 2 H), 3.57 (s, 4 H, NH₂). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ = 184.0, 158.2, 149.9, 146.1, 145.4, 139.8, 133.8, 131.6, 131.3, 131.0, 127.9, 127.1, 121.6, 116.2, 115.3, 56.8. Elem. Anal. Calcd. for $\text{C}_{38}\text{H}_{28}\text{N}_2\text{O}_3$: C 81.41%, H 5.03%, N 5.00%; found C 81.83%, H 5.22%, N 4.85%. FTIR (KBr): ν_{max} = 3469, 3369 (N–H stretching), 3036, 1648 (Ar–CO–Ar stretching), 1598, 1497, 1319 (C–N stretching), 1233 (Ar–O–Ar stretching), 1168 and 1011 (Ar–O–Ar stretching), 932, 875, 832, 746 cm^{-1} .

Preparation of polymer films

The preparation process of representative polyimide (PI-6c) is as follows. To a stirred solution of **BAPA (3)** (1.6820 g, 1.5 mmol) in DMAc (3 mL), was added **ODPA (5c)** (0.4653 g, 1.5 mmol) in one portion. Extra 3 mL of DMAc was then added to adjust the solid content 15 wt%. The mixture was stirred in ice bath for 1 h and then stirred at room temperature for 10 h under nitrogen atmosphere to form the poly(amic acid) (PAA-5c). From this solution a PAA film was cast onto a flat and clean glass plate and heated by a stepped thermal sequence (80 °C/8 h, 150 °C/1 h, 200 °C/1 h, 250 °C/1 h, and 300 °C/2 h) under vacuum to convert the PAA-5c into the polymer film (PI-6c).

Chemical imidization was performed by adding extra DMAc, and an equimolar mixture of acetic anhydride and pyridine into the above-mentioned PAA-5c solution with stirring at room temperature for 1 h, and then heating at 100 °C for 3 h. After the reaction, the mixture was poured into methanol and the pale-yellow solid precipitate was filtered, washed with methanol and hot water successively, and then dried at 110 °C for 12 h to afford PI-6c. All other polyimides were prepared using a similar procedure.

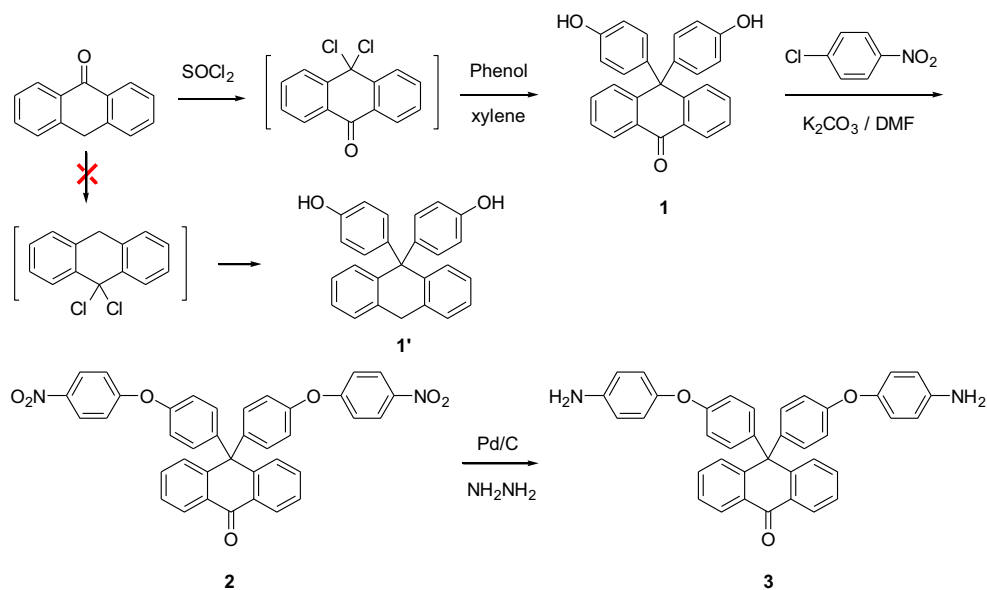
Results and discussion

Synthesis of intermediates and monomer

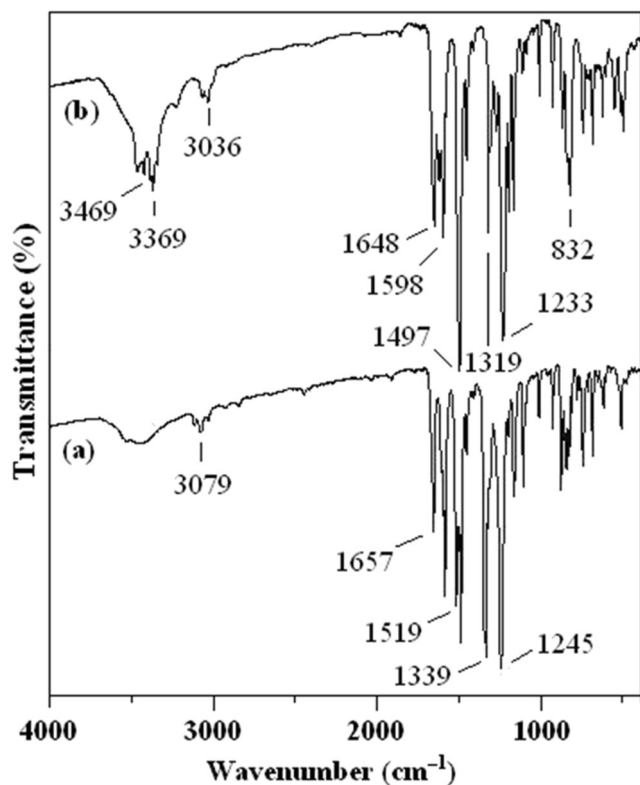
Scheme 1 illustrated a synthesis route to the new diamine monomer (**3**), 10,10-bis[4-(4-aminophenoxy)phenyl]-9(10H)-anthrone (**BAPA**). First, 10,10-bis(4-hydroxyphenyl)-9(10H)-anthrone (**1**) was prepared in 85% yield via one-pot, two-step synthetic procedure by reaction of 9(10H)-anthrone with thionyl chloride, affording 10,10-dichloro-9(10H)-anthrone, without isolating this compound, followed by treatment with phenol in refluxing xylene, according to our reported similar method [24]. It should be noted that an expected compound, 9,9-bis(4-hydroxyphenyl)-9,10-dihydroanthracene (**1'**) was not obtained under the above conditions. This may be due to the fact that the activity of carbonyl group is lower than that of benzyl group in 9(10H)-anthrone. Second, the aromatic substitution of bisphenol intermediate (**1**) and 4-chloronitrobenzene in the presence of potassium carbonate produced the dinitro compound (**2**), 10,10-bis[4-(4-nitrophenoxy)phenyl]-9(10H)-anthrone. Third, conversion of **2** to **3** was accomplished by reduction using hydrazine monohydrate and a catalytic amount of palladium on activated carbon in refluxing ethanol.

The structures of compounds (**1**, **2** and **3**) were confirmed by elemental analysis, FTIR, and NMR spectroscopy. As depicted in *Experimental section*, the elemental analysis data of all compounds were found to correspond well with the calculated values for their structures.

The hydrogenation of **2** to **3** was monitored by FTIR spectroscopy (Fig. 1), in which, the dinitro compound (**2**) displayed two characteristic bands at 1519 cm^{-1} (asymmetric stretching) and 1339 cm^{-1} (symmetric stretching) related to the nitro groups (Fig. 1a), whereas the diamine (**3**) had no these absorption peaks, but showed new absorptions at 3469 and 3369 (N–H stretching) (Fig. 1b). In addition, when the nitro group is converted to amino group, the characteristic stretching vibrations of the carbonyl and aryl ether groups shifted from 1657 and 1245 cm^{-1} to 1648 and 1233 cm^{-1} due to the different electronic effects of substituents, respectively. Both **2** and **3** were assigned with each carbon and proton in their ^1H NMR and ^{13}C NMR spectra, respectively.

Scheme 1 Synthesis of the diamine (**3**)

The typical NMR spectra of the diamine (**3**) were shown in Fig. 2. As can be seen, almost all aromatic protons except for H^c and H^g were clearly distinguished (Fig. 2a). The ¹³C NMR spectrum (Fig. 2b) showed 16 carbons signals, which appeared in the region of 184.0–56.8 ppm. Especially, the carbonyl carbon C¹ and aliphatic carbon C⁸ indicated a singlet at 184.0 and 56.8 ppm, respectively.

**Fig. 1** FTIR spectra of the dinitro compound **2** (a) and the diamine **3** (b)

Polymer synthesis

As outlined in Scheme 2, a series of new 9(10H)-anthrone-tape cardo polyimides (**6a–6f**) were prepared by the conventional two-step polymerization method, which involved ring-opening polyaddition forming PAAs and subsequent thermal imidization or chemical cyclodehydration. In all case, the polymerization was carried out effectively at ambient temperature for 10–12 h to afford viscous PAA solution by reacting equimolar amounts of **BAPA** (**3**) with commercially available aromatic dianhydrides (**4a–4f**) (**PMDA**, **BPDA**, **ODPA**, **BTDA**, **SDPA** and **6FDA**) at a concentration of approximately 15% solids in DMAc.

Table 1 presented the inherent viscosities of the PAAs (**5a–5f**) in the range 0.91–1.53 dL/g and elemental analysis data of the resulting PIs (**6a–6f**). The PAA films were then thermally imidized at temperatures up to 300 °C under vacuum to produce flexible and transparent polyimide films. Alternatively, adding dehydrating agents, acetic anhydride and pyridine to the PAAs achieved chemical imidization to obtain the corresponding polyimides. Furthermore, the THF-soluble PI (**6f**) prepared by chemical imidization method exhibited weight-average molecular weight (M_w) and number-average molecular weight (M_n) of 55,800 and 26,500, respectively, with the polydispersity index (M_w/M_n) value of 2.1, as determined by gel permeation chromatography (GPC) compared to the polystyrene standard using THF as the eluent.

The identification of imidization of PAAs to PIs was made by FTIR spectra. Figure 3 compared the typical FTIR spectra of PAA-**5c** and the related PI-**6c** obtained by thermal cyclodehydration. As shown in Fig. 3a, The PAA-**5a** exhibited major absorption peaks at 1715, 1658, 1535 and 1236 cm⁻¹, belonged to carbonyl stretch of the carboxylic acid, carbonyl stretch of anthrone units, N–H stretch of amide II mode, and C–O–C stretch of aryl ether group, respectively. Figure 3b showed characteristic bands at 1777 (asymmetrical C=O stretch)

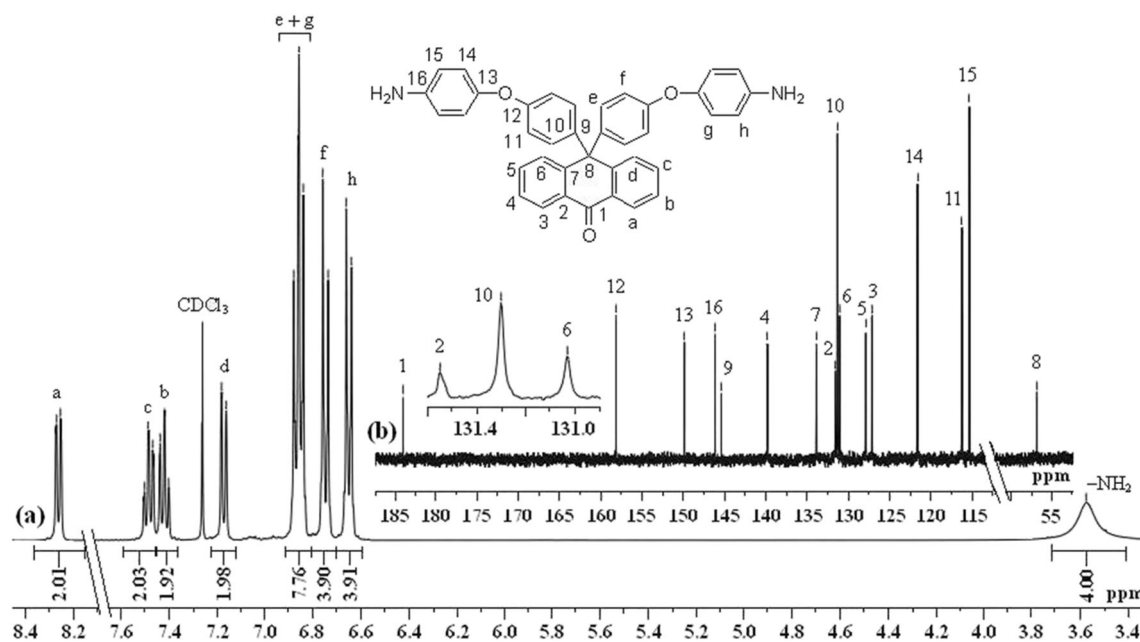


Fig. 2 ^1H (a) and ^{13}C (b) NMR spectra of the diamine (3)

Scheme 2 Preparation of the PIs (6a–6f)

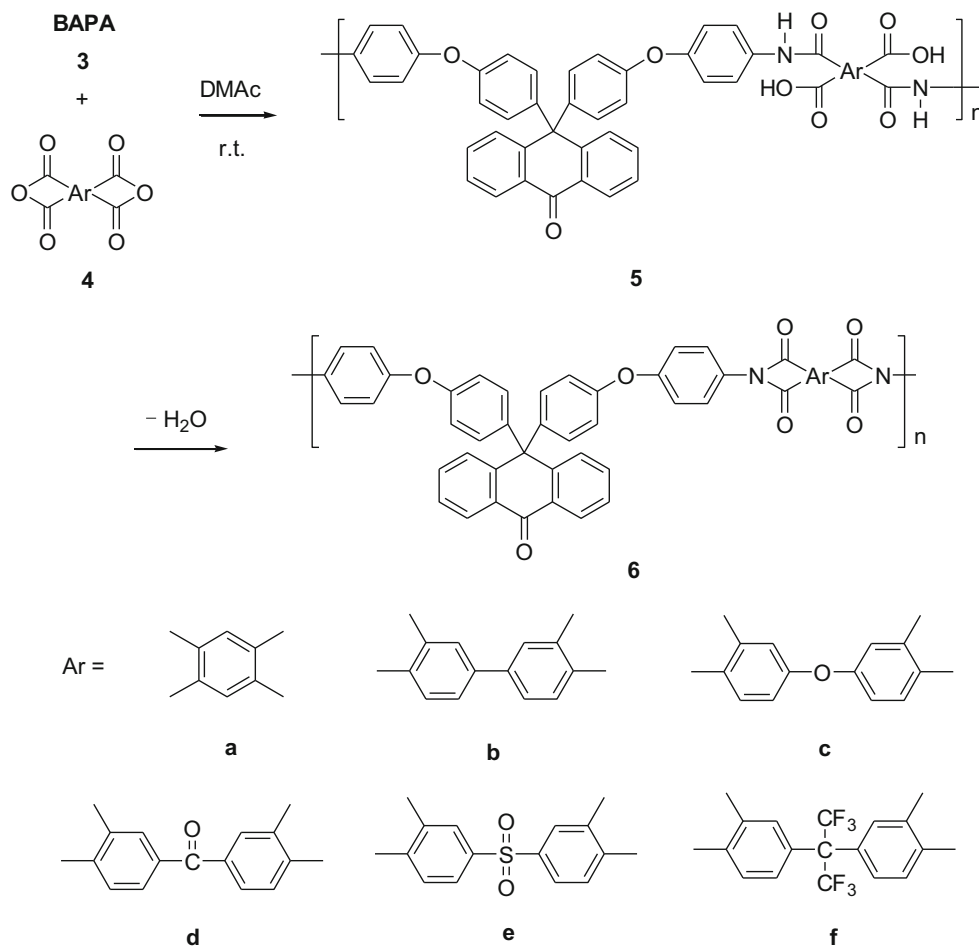
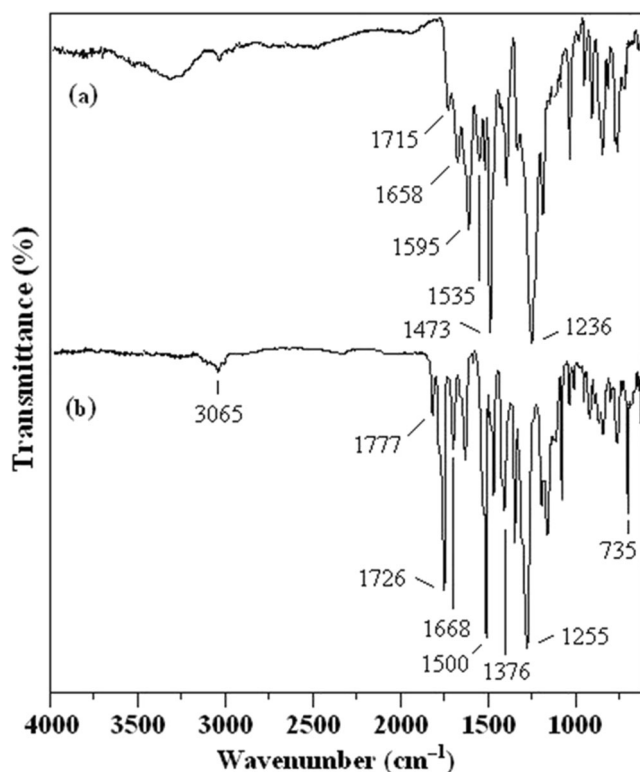


Table 1 Inherent viscosity of the PAAs and elemental analysis of PIs

PAAs (5a–5f)		Elemental analysis (%) of PIs (6a–6f) ^b					
Code	η_{inh} (dL/g) ^a	Code	Formula of the repeat unit (molecular weight)		C	H	N
5a	1.53	6a	(C ₄₈ H ₂₆ N ₂ O ₇) _n (742.74) _n	Cacld.	77.62	3.53	3.77
				Found	76.45	3.59	3.82
				Found	(77.21)	(3.64)	(3.86)
5b	1.35	6b	(C ₅₄ H ₃₀ N ₂ O ₇) _n (818.84) _n	Cacld.	79.21	3.69	3.42
				Found	78.02	3.76	3.49
				Found	(78.86)	(3.83)	(3.53)
5c	0.91	6c	(C ₅₄ H ₃₀ N ₂ O ₈) _n (834.84) _n	Cacld.	77.69	3.62	3.36
				Found	76.76	3.77	3.41
				Found	(77.22)	(3.84)	(3.46)
5d	1.08	6d	(C ₅₅ H ₃₀ N ₂ O ₈) _n (850.85) _n	Cacld.	76.23	3.55	3.29
				Found	75.51	3.62	3.36
				Found	(75.95)	(3.67)	(3.39)
5e	1.18	6e	(C ₅₄ H ₃₀ N ₂ O ₉ S) _n (882.91) _n	Cacld.	73.46	3.43	3.17
				Found	72.22	3.51	3.23
				Found	(72.88)	(3.54)	(3.26)
5f	1.26	6f	(C ₅₇ H ₃₀ F ₆ N ₂ O ₇) _n (968.86) _n	Cacld.	70.66	3.12	2.89
				Found	69.24	3.22	2.94
				Found	(69.83)	(3.27)	(2.98)

^a Measured at a concentration of 0.5 g/dL in DMAc at 30 °C^b Data in parentheses are for the PIs by chemical imidization**Fig. 3** FTIR spectra of PAA-**5c** (a) and the corresponding PI-**6c** (b)**Table 2** Solubility of the PIs prepared by thermal or chemical imidization^a

Code	NMP	DMAc	DMF	DMSO	Py	<i>m</i> -Cresol	THF	CHCl ₃
PI- 6a	--	--	--	--	--	--	--	--
	(--)	(--)	(--)	(--)	(--)	(--)	(--)	(--)
PI- 6b	--	--	+--	--	--	--	--	--
	(++)	(++)	(++)	(--)	(++)	(++)	(--)	(--)
PI- 6c	++	++	++	--	++	++	--	--
	(++)	(++)	(++)	(++)	(++)	(++)	(+h)	(--)
PI- 6d	--	--	+--	--	--	--	--	--
	(++)	(++)	(++)	(--)	(--)	(++)	(--)	(--)
PI- 6e	+--	+--	++	+--	--	++	--	--
	(++)	(++)	(++)	(--)	(++)	(++)	(--)	(--)
PI- 6f	++	++	++	++	++	++	+h	--
	(++)	(++)	(++)	(++)	(++)	(++)	(++)	(--)

^a Tested with 10 mg polymer sample in 1 mL solvent with stirring. Data in parentheses are the solubility of the PIs by chemical imidization. ++ = soluble at room temperature; +-- = partial soluble at room temperature; +h = soluble on heating 60 °C; -- = insoluble. NMP: *N*-methyl-2-pyrrolidone; DMAc: *N,N*-dimethylacetamide; DMF: *N,N*-dimethylformamide; DMSO: dimethylsulfoxide; Py, Pyridine; THF: tetrahydrofuran

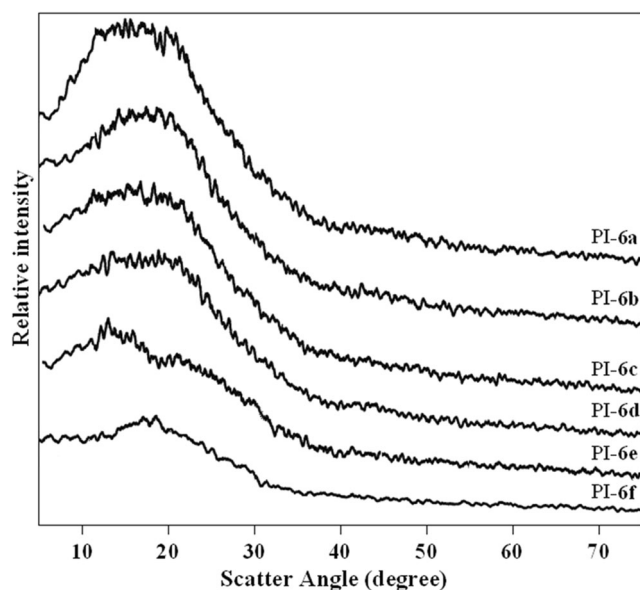


Fig. 4 WAXD patterns of the PIs (**6a–6f**)

and 1726 cm^{-1} (symmetrical C=O stretch) of carbonyl group of imide, as well as 735 cm^{-1} (flexural vibration of imide ring). Besides, the C–N band at 1376 cm^{-1} also confirmed the formation of the imide structure. On the other hand, as shown in Table 1, the elemental analysis values of the resulting polyimides were generally in good agreement with their respective structures for hydrogen and nitrogen, while the carbon analyses were below their theoretical values—a phenomenon common to high-temperature polyimides.

Solubility and crystallinity

The solubility of the PI samples (**6a–6f**) was tested qualitatively in various solvents, and the results were listed in Table 2. On the whole, the polyimides prepared by the

chemical conversion method had better solubility compared with those by the thermal procedure. PI-**6a**, derived from PMDA obtained by both thermal and chemical imidization is insoluble in the tested solvent, whereas PI-**6f**, based on 6FDA is soluble in most solvents such as NMP, DMF, DMAc, DMSO, *m*-cresol and pyridine, even in low boiling point solvent like THF at room temperature, which is attributed to the additional contribution of the flexible ether linkages and hexafluoroisopropylidene units in its main chains.

Compared with the PIs prepared from the two-step thermal imidization, PI-**6b**, PI-**6c**, PI-**6d** and PI-**6e** prepared from the chemical imidization method exhibited better solubility, which was attributed to the aggregation of the polymer chain segments during heat treatment. Therefore, the excellent solubilities render these PIs as promising candidates to fabricate large area devices by solution process.

The wide-angle X-ray diffraction (WAXD) studies of these polymers (Fig. 4) indicated that all of the prepared PIs (**6a–6f**) were completely amorphous. This result was mainly attributed to the introduction of the bulky pendant 9(10*H*)-anthrone groups, which hindered packing of the polymer chain and decreased the intermolecular forces between the polymer chains, subsequently causing a decrease in crystallinity. In addition, the presence of the flexible ether group certainly reduced the rigidity of the polymer chains. In general, most cardo polymers are amorphous owing to the bulky pendant structure, which often reflected their good solubility.

Mechanical properties

Table 3 summarized the tensile properties of the present PI films prepared by the thermal conversion method. The films had tensile strength of 79.6–115.2 MPa, elongation at break of 10.8–21.7%, and tensile modulus of 1.97–2.48 GPa, indicating that they were strong and hard materials.

Table 3 Thermal and tensile properties of the PIs ^a

Code	T_g (°C) ^b	T_{d10} (°C) ^c	R_w (%) ^d	T_s (MPa) ^e	E_b (%) ^f	T_m (GPa) ^g
PI- 6a	359 (353)	544 (548)	65 (63)	87.7	21.2	2.26
PI- 6b	324 (321)	566 (568)	63 (61)	115.2	10.8	2.48
PI- 6c	290 (291)	556 (550)	65 (64)	95.4	21.7	2.29
PI- 6d	311 (311)	560 (562)	64 (62)	110.6	17.8	2.36
PI- 6e	321 (322)	522 (520)	59 (58)	82.1	11.5	2.18
PI- 6f	318 (317)	536 (542)	64 (63)	79.6	12.8	1.97
7 [16]	291	575	64	67	7	2.07
8 [18]	260	523	58	98	8	2.10
9 [24]	286	570	60	94	9	2.27

^a Data in parentheses are the thermal property of the PIs by chemical imidization

^b Glass-transition temperature from the second heating trace of DSC measurements

^c The decomposition temperature at a 10% weight loss in nitrogen

^d Residual weight percentage at 800 °C in nitrogen

^e Tensile strength

^f Elongation at break

^g Tensile modulus

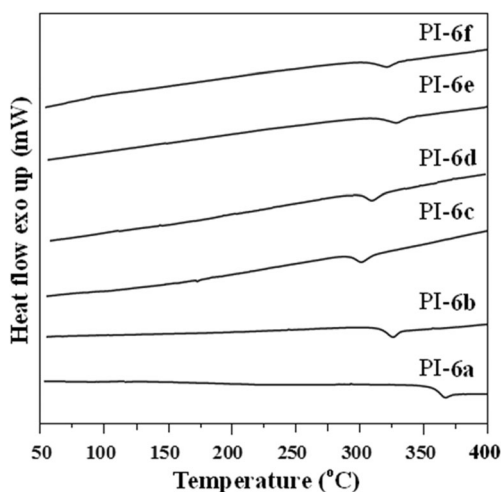


Fig. 5 DSC curves of the PIs (**6a–6f**)

Thermal property

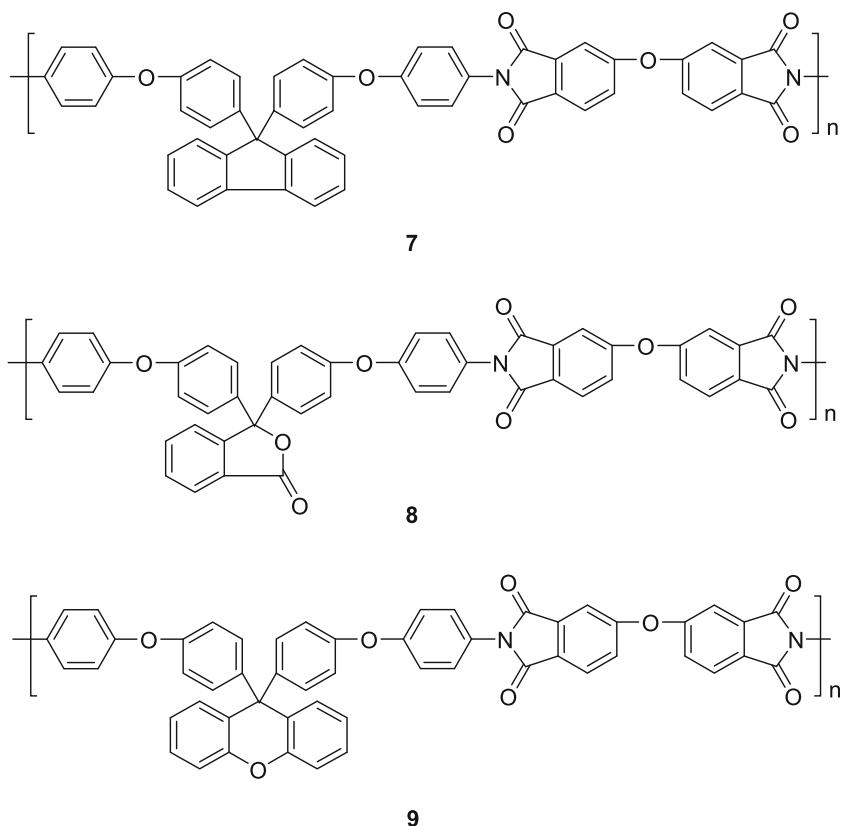
The thermal properties of the resulting PIs (**6a–6f**) were tabulated in Table 3. Their T_g 's, determined by means of differential scanning calorimeter (DSC), were found to be in the range of 290–359 °C. As shown in Fig. 5, no crystallization or melting peaks were observed from the DSC curves, which supported the generally amorphous of polymers and agreed well with the WAXD results. As expected, PI-**6c** obtained from

ODPA (**4c**) had the lowest T_g (290 °C) as a result of the presence of more flexible ether linkages, while pyromellitimide-containing PI-**6a** exhibited the highest one (359 °C) owing to its most rigid polymer backbones. The relatively high T_g (321 °C) of PI-**6e** could be owing to the polar sulfonyl group incorporated in the main chains.

The thermal stability of these PIs (**6a–6f**) was evaluated by thermogravimetric (TG) analysis. It was found that all of the prepared polyimides did not lose weight below 500 °C in nitrogen. As seen from Table 3, the temperatures (T_{d10}) at 10% weight loss were in the range of 522–566 °C, and their char yields at 800 °C were above 59%, implying that the present PIs possess excellent thermal stability. It should be noted that, among them, the SDPA-derived PI-**6e** had the lowest decomposition temperature and char yield than the other analogues, possibly due to the degradation of the less stable sulfonyl groups. In fact, similar results were reported in literatures [6, 11, 16, 18].

As shown in Scheme 3 and Table 3, in contrast, the thermal and tensile properties of the present corresponding PI-**6c** are comparable to those of the analogous cardo polyimides (**7**) [16], (**8**) [18] and (**9**) [24], prepared from 1,1-bis[4-(4-aminophenoxy)phenyl]fluorine, 1,1-bis[4-(4-aminophenoxy)phenyl]phthalide and 2,2-bis[4-(4-aminophenoxy)phenyl]xanthene with **OPDA**, respectively.

Scheme 3 The structures of three analogous cardo PIs (**7**), (**8**) and (**9**)



Conclusions

10,10-Bis[4-(4-aminophenoxy)phenyl]-9(10*H*)-anthrone was successfully synthesized, and reacted with various aromatic dianhydrides to yield a series of novel 9(10*H*)-anthrone-type cardo PIs by two-step polycondensation method. The introduction of flexible ether and bulky pendant 9(10*H*)-anthrone groups into the polymer backbone simultaneously resulted in the polyimides with excellent thermal and mechanical properties, and good solubility in common organic solvents. These characteristics indicate that the present PIs could be considered as new candidates for processable high performance materials, and has potential application in microelectronic manufacturing, the packaging industry and so on.

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