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# Synthesis and characterization of novel polyimides based on 10,10-bis[4-(4-aminophenoxy)-3-methylphenyl]-9(10*H*)-anthrone

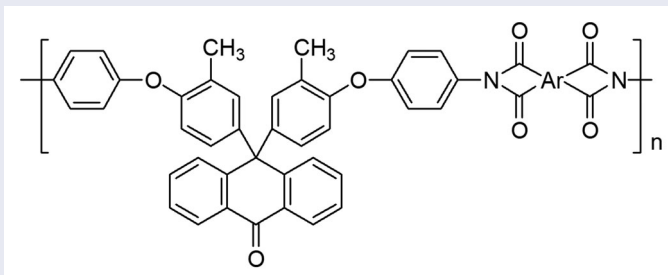
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## ABSTRACT

10,10-Bis[4-(4-aminophenoxy)-3-methylphenyl]-9(10*H*)-anthrone, as a novel aromatic diamine, was synthesized from anthrone by three-step process. A series of polyimides containing methyl substituents and 9(10*H*)-anthrone pendant groups was prepared from this diamine with various aromatic dianhydrides *via* the poly(amic acid) (PAA) precursors and subsequent thermal or chemical imidization procedure. Inherent viscosities of PAAs are between 0.87 and 1.58 dL/g, and the corresponding polyimides have the weight-average molecular weight and number-average molecular weight in the range of 49,400–64,200 and 28,700–37,700, respectively. Most of the polyimides obtained through the chemical cyclodehydration method are soluble in NMP, DMF, DMAc, Py and *m*-cresol at room temperature. These polyimides have glass transition temperatures of 289–313 °C, 10% weight loss temperatures of 484–524 °C, char yields of 55–63% at 800 °C, and temperature at the maximum-rate degradation of 560–584 °C in nitrogen, respectively. The polyimide films obtained through the thermal imidization have tensile strength of 76.43–119.74 MPa, elongation at break of 6.93–12.33%, and tensile modulus of 1.91–2.38 GPa.

## GRAPHICAL ABSTRACT



## ARTICLE HISTORY

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## KEYWORDS

Aromatic polyimides; 10,10-bis[4-(4-aminophenoxy)-3-methylphenyl]-9(10*H*)-anthrone; bulky pendant groups; ether linkages; methyl substituents; synthesis and properties

## 1. Introduction

Aromatic polyimides, as important high-performance polymers, have been noted for their high thermal and mechanical properties, as well as chemical resistance.<sup>[1–3]</sup> However, their extensive application is often limited by processing difficulty due to their poor solubility in organic solvents and high processing temperature, which are caused by rigid polymer backbone and the strong interchain interaction. In order to overcome these problems, different structural modification has been carried out to improve their solubility and processing characteristics. Among them, incorporation of flexible linkages such as O, S, SO<sub>2</sub>, CH<sub>2</sub>, (CH<sub>3</sub>)<sub>2</sub>C, (CF<sub>3</sub>)<sub>2</sub>C or R<sub>2</sub>Si into polymer backbone has been generally recognized as a useful and convenient method for improving their solubility and processability.<sup>[4–14]</sup> But, the flexible groups usually tend to lower the thermal stability and even mechanical property of the polymer to a certain extent. Therefore,

ideal structure modification of polymer is expected to provide balanced properties of high thermal stability and good processability. Classically, a polymer chain with cyclic side groups (usually named as cardo groups) such as fluorene,<sup>[15–18]</sup> phthalide,<sup>[19,20]</sup> cyclohexylidene,<sup>[21]</sup> adamantine,<sup>[22]</sup> or xanthene,<sup>[23,24]</sup> *etc.* could possess high glass transition temperature (*T<sub>g</sub>*), good thermal-resistance and mechanical properties, as well as excellent solubility in organic solvents. The 9(10*H*)-anthrone group could be considered as a cardo group and was previously inserted into several polymer backbones such as polyarylates and poly(1,3,4-oxadiazole)s derived from 10,10-bis(4-carboxyphenyl)-9(10*H*)-anthrone, as well as polyamides and polyimides based on 10,10-bis(4-aminophenyl)-9(10*H*)-anthrone to improve the processability.<sup>[25]</sup> This indicated that the introduction of cardo 9(10*H*)-anthrone group into the polymer backbone would be a potential modification to the

structure of rigid polymers. In addition, solubility of polyimides can also be improved by incorporation of less symmetric structures such as *ortho*- and *meta*-methyl substituted aromatic units in the main chain.<sup>[26–28]</sup> Moreover, it was also found that the incorporation of methyl substituents into phenylene units can enhance the thermooxidative stability of polymers.<sup>[29]</sup> Therefore, introducing flexible ether segments, cardo bulky pendent groups and unsymmetrical moieties simultaneously into the main chain of the polymer is expected to improve the solubility of the polymer, while retaining its good thermal stability. However, there are few literatures on the characteristic of polyimides derived from the monomers containing ether, methyl and 9(10*H*)-anthrone groups. As part of an ongoing research program focused on the use anthrone as a starting material in the development of high performance polymer,<sup>[30]</sup> we report herein a series of new cardo aromatic polyimides bearing methyl and 9(10*H*)-anthrone pendant groups based on a new diamine, 10,10-bis[4-(4-aminophenoxy)-3-methylphenyl]-9(10*H*)-anthrone. The new prepared poly(ether imide)s are expected to have good processability and thermal properties. In this study, the general properties such as solubility, crystallinity, tensile and thermal properties of the polymers were also investigated.

## 2. Experimental

### 2.1. Materials

All chemicals such as anthrone, *o*-cresol, 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**), 4,4'-oxydiphthalic anhydride (ODPA, **4b**), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA, **4c**), 4,4'-sulfonyldiphthalic anhydride (SDPA, **4d**), and 4,4'-hexafluoroisopropylidenediphthalic anhydride (6FDA, **4e**) were recrystallized from acetic anhydride. Xylene was refluxed with sodium and distilled under reduced pressure. *N,N*-Dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc) and *N*-methyl-2-pyrrolidone (NMP) were purified by distillation under reduced pressure over calcium hydride. Potassium carbonate was dried *in vacuo* at 130 °C for 12 h.

### 2.2. Measurements

<sup>1</sup>H (400 MHz) and <sup>13</sup>C (100 MHz) NMR spectra were recorded on Bruker Avance 400 MHz spectrometer using deuterated chloroform (CDCl<sub>3</sub>) or dimethyl sulfoxide-*d*<sub>6</sub> (DMSO-*d*<sub>6</sub>) as solvent with tetramethylsilane (TMS) as an internal standard. FTIR spectra of the intermediates and monomer in KBr pellets, and polymer films were determined on a Perkin-Elmer SP One Fourier-transform infrared (FTIR) spectrometer. Microanalyses were run in a Euro Vector EA3000 Elemental Analyzer. DSC traces were measured on a Perkin-

Elmer DSC-7 instrument at the rate of 20 °C/min in flowing nitrogen (30 cm<sup>3</sup>/min). The second scan was immediately initiated after the sample was cooled to room temperature. The glass transition temperature (*T*<sub>g</sub>) values were reported from the second scan after the first heating and quenching, and taken from the midpoint of the change in the slope of the baseline. Thermogravimetry analysis (TGA) and differential thermal gravity (DTG) were conducted with a Perkin-Elmer Diamond TG-DTA instrument, and experiments were carried out on approximately 5 mg samples heated in flowing nitrogen 50 mL/min at a heating rate of 10 °C/min. Weight- and number-average molecular weights of each synthesized polymer were obtained *via* gel permeation chromatography (GPC) based on a polystyrene calibration using a Waters 510 HPLC equipped with four Waters columns measuring 300 mm 37.7 mm (10<sup>2</sup>, 10<sup>3</sup>, 10<sup>4</sup>, and 10<sup>5</sup> Å in a series) connected in series and a UV detector at 254 nm using DMF (1 mL/min) as eluent. Wide-angle X-ray diffraction (WAXD) patterns were recorded at room temperature (about 25 °C) on a Rigaku Geiger Flex D-Max IIIa X-ray diffractometer, using Ni-filtered CuK<sub>α</sub> radiation (operating at 40 kV and 15 mA); the scanning rate was 2°/min over a range of 2θ = 5–80°. The stress-strain behavior of the polymer films were measured on an Instron 1122 testing instrument with a load cell of 5 kg at a crosshead speed of 5 mm/min on strips (0.5 cm wide, 6 cm long, and about 0.05 mm thick), and an average of at least four individual determinations was used. The inherent viscosities were measured at 0.5 g/dL concentration in NMP or DMAc with an Ubbelohde viscometer at 30 °C, in which the polymer samples were pretreated by drying in oven at 120 °C for 1 h to remove the adsorbed moisture.

### 2.3. Synthesis of intermediate and monomer

**10,10-Bis(4-hydroxy-3-methylphenyl)-9(10*H*)-anthrone (1):** A mixture of anthrone (9.7 g, 50 mmol) and thionyl chloride (30 mL) was refluxed for 6 h. After removing the excess of thionyl chloride under vacuum, *o*-cresol (16.2 g, 150 mmol) and xylene (40 mL) were added to the reaction mixture, which was stirred at 115 °C for 7 h. After the reaction, excess *o*-cresol 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 white solid (**1**) (16.9 g, 83%); mp = 249–250 °C (determined by DSC). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ = 9.36 (s, 2 H), 8.11 (d, *J* = 8.0 Hz, 2 H), 7.59 (t, *J* = 7.6 Hz, 2 H), 7.47 (t, *J* = 7.4 Hz, 2 H), 7.19 (d, *J* = 7.6 Hz, 2 H), 6.66 (d, *J* = 8.4 Hz, 2 H), 6.60 (s, 2 H), 6.55 (d, *J* = 8.0 Hz, 2 H), 1.97 (s, 6 H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ = 184.3, 154.5, 150.8, 137.1, 133.5, 132.2, 131.6, 131.1, 128.5, 127.5, 126.9, 123.8, 114.5, 56.8, 16.8. Elem. Anal. Calcd. for C<sub>28</sub>H<sub>22</sub>O<sub>3</sub>: C 82.74%, H 5.46%, found C 82.96%, H 5.59%. FTIR (KBr): ν<sub>max</sub> = 3068, 3324, 1664 (Ar–CO–Ar stretching), 1600, 1513, 1441, 1332, 1234, 1180, 933, 825, 739, 688 cm<sup>−1</sup>.

**10,10-Bis[4-(4-nitrophenoxy)-3-methylphenyl]-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 the dinitro compound (**1**) (4.06 g, 10 mmol),  $K_2CO_3$  (3.45 g, 10 mmol), 4-chloronitrobenzene (3.15 g, 20 mmol) in anhydrous DMF (60 mL) was heated and refluxed for 6 h. After which, the reaction mixture was cooled to room temperature, and poured into 100 mL of methanol/water (1:1). The yellow crude product was collected by filtration, washed thoroughly with water, dried in vacuum, and recrystallized from petroleum ether/dichloromethane to give light-yellow needle crystals (**2**) (5.57 g, 86%); mp = 218–219 °C (determined by DSC).  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  = 8.33 (d,  $J$  = 8.0 Hz, 2 H), 8.18 (d,  $J$  = 8.4 Hz, 4 H), 7.58 (t,  $J$  = 7.4 Hz, 2 H), 7.50 (t,  $J$  = 7.6 Hz, 2 H), 7.21 (d,  $J$  = 7.6 Hz, 2 H), 6.94–6.88 (m, 10 H), 2.07 (s, 6 H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  = 184.5, 162.9, 151.4, 148.9, 143.6, 142.6, 133.6, 132.8, 132.4, 130.5, 130.1, 129.5, 127.7, 127.6, 126.0, 120.3, 116.3, 57.5, 16.4. Elem. Anal. Calcd. for  $C_{40}H_{28}N_2O_7$ : C 74.07%, H 4.35%, N 4.32%, found C 74.41%, H 3.46%, N 4.18%. FTIR (KBr):  $\nu_{max}$  = 3068, 2924, 1650 (Ar–CO–Ar stretching), 1593, 1491, 1521 and 1340 ( $NO_2$  stretching), and 1253 (Ar–O–Ar stretching), 1158 and 1122 (Ar–O–Ar stretching), 847, 745  $cm^{-1}$ .

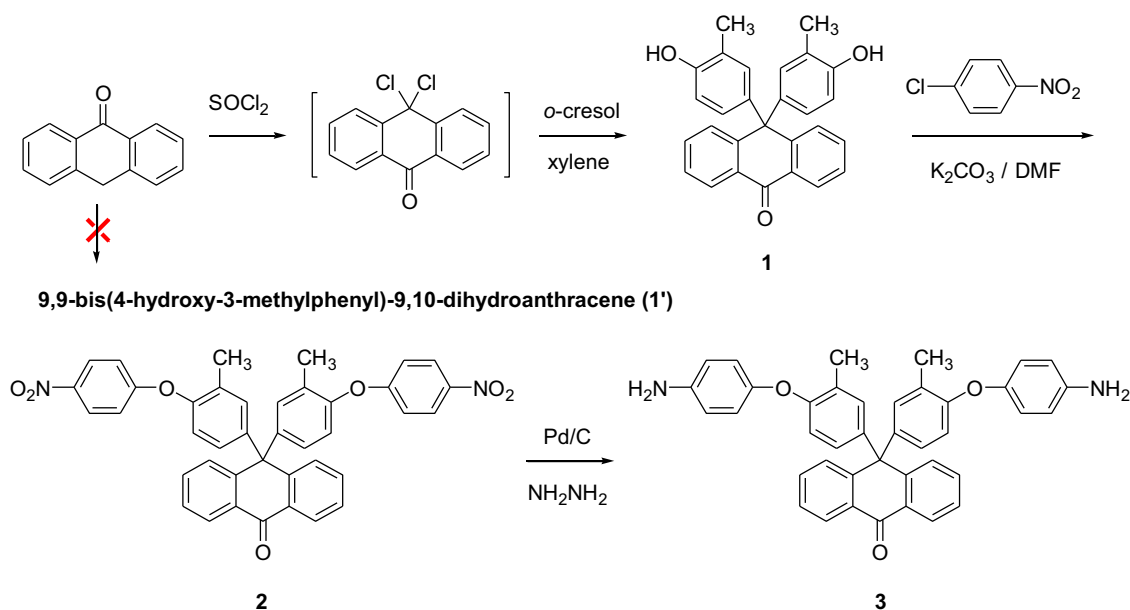
**10,10-Bis[4-(4-aminophenoxy)-3-methylphenyl]-9(10H)-anthrone (**3**):** A mixture of the dinitro compound (**2**) (9.73 g, 15 mmol), anhydrous ethanol (100 mL), and a catalytic amount of 10% Pd/C (0.1 g) was added to a 250 mL three-necked flask equipped with a dropping funnel and a reflux condenser. 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 crystal (**3**) (7.77 g, 88%); mp = 232–233 °C (determined by DSC).  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  = 8.28 (d,  $J$  = 7.6 Hz, 2 H), 7.49 (t,  $J$  = 7.6 Hz, 2 H), 7.43 (t,  $J$  = 7.4 Hz, 2 H), 7.20 (d,

$J$  = 7.6 Hz, 2 H), 6.79–6.77 (m, 6 H), 6.67–6.62 (m, 6 H), 6.56 (d,  $J$  = 8.4 Hz, 2 H), 3.54 (s, 4 H,  $NH_2$ ), 2.15 (s, 6 H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  = 184.8, 155.3, 149.9, 149.0, 142.3, 140.2, 132.8, 132.6, 132.2, 130.7, 128.6, 127.6, 127.2, 127.1, 120.3, 116.2, 115.8, 57.2, 16.6. Elem. Anal. Calcd. for  $C_{40}H_{32}N_2O_3$ : C 81.61%, H 5.48%, N 4.76%; found C 81.98%, H 5.59%, N 4.91%. FTIR (KBr):  $\nu_{max}$  = 3438, 3365 (N–H stretching), 3068, 1665 (Ar–CO–Ar stretching), 1599, 1491, 1317 (C–N stretching), 1238 (Ar–O–Ar stretching), 1122, 934, 825  $cm^{-1}$ .

## 2.4. Preparation of polyimide films

The preparation process of representative polyimide (PI-**6a**) is as follow. To the stirred solution of the diamine (**3**) (2.00 mmol, 1.1774 g) in DMAc (4 mL), was added PMDA (**4a**) (0.4362 g, 2.0 mmol) in one portion. Extra 4 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-**5a**). 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 form the polyimide film (PI-**6a**). FTIR (film):  $\nu_{max}$  = 1770 and 1730  $cm^{-1}$  (C=O stretching), and 1377  $cm^{-1}$  (C–N stretching).

Chemical imidization was carried out by adding extra DMAc, and an equimolar mixture of acetic anhydride and pyridine into the above-mentioned PAA-**5a** 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 100 °C under vacuum. The inherent viscosity of the chemically imidized polyimide was 1.22 dL/g in NMP with a 0.5 g/dL concentration at 30 °C. All other polyimides were prepared with an analogous procedure.



Scheme 1. Synthesis route for the preparation of the diamine (**3**).

### 3. Results and discussion

#### 3.1. Monomer synthesis

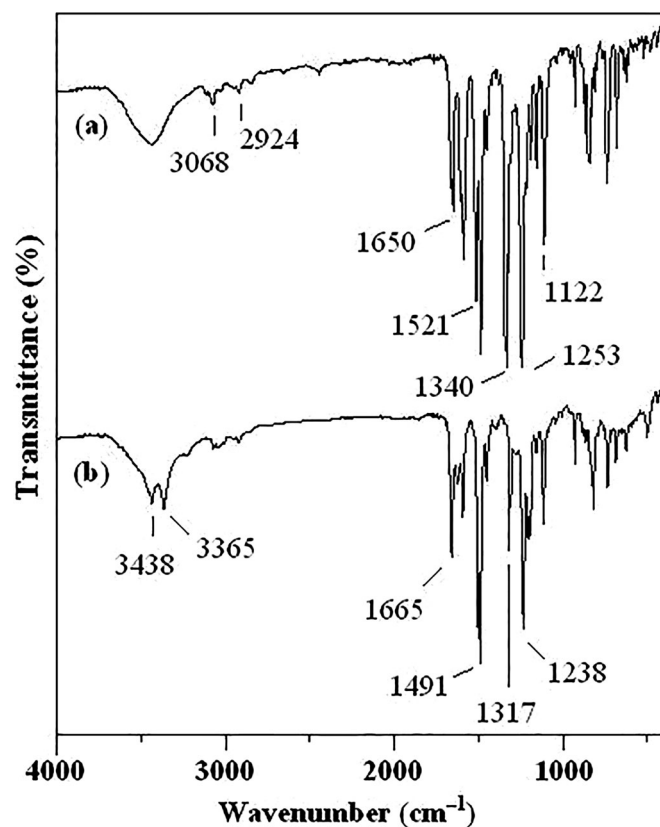
**Scheme 1** outlined the synthetic route for the preparation of the new diamine, 10,10-bis[4-(4-aminophenoxy)-3-methylphenyl]-9(10*H*)-anthrone (**3**, **BAMPA**). First, 10,10-bis(4-hydroxy-3-methylphenyl)-9(10*H*)-anthrone (**1**) was prepared in good yield *via* one-pot, two-step synthetic procedure by reaction of anthrone with thionyl chloride, affording 10,10-dichloro-9(10*H*)-anthrone, followed by treatment with *o*-cresol in refluxing xylene using a similar method.<sup>[23]</sup> But, the expected product, 9,9-bis(4-hydroxy-3-methylphenyl)-9,10-dihydroanthracene (**1B**) was not obtained under the same conditions. Second, reaction of bisphenol intermediate (**1**) with 4-chloronitrobenzene in the presence of potassium carbonate afforded the dinitro compound, 10,10-bis[4-(4-nitrophenoxy)-3-methylphenyl]-9(10*H*)-anthrone (**2**). Third, conversion the dinitro compound (**2**) to the diamine (**3**) was completed by catalytic reduction with hydrazine monohydrate and a catalytic amount of palladium on activated carbon in refluxing ethanol.

The structures of these compounds were confirmed by elemental analysis, FTIR, and NMR spectroscopy. As described in Experimental section, the element analysis data of each compound were in good agreement with the calculated values for its structure. As shown in **Figure 1**, when the dinitro compound (**2**) was reduced to the diamine (**3**), two characteristic bands of nitro group disappeared and the absorption peaks of amino groups (3438 and 3365 cm<sup>-1</sup>) appeared evidently. The NMR spectra of the diamine (**3**) were depicted in **Figure 2**. As observed, assignment of each proton was given in the **Figure 2a**. Almost all aromatic protons except for H<sup>e</sup> and H<sup>g</sup> were clearly distinguished. The <sup>13</sup>C-NMR spectrum (**Figure 2b**) exhibited 19 peaks of various absorptions for every carbon, which appeared in the region of 184.8–16.6 ppm. Especially, the carbonyl carbon C<sup>1</sup> and methyl carbon C<sup>19</sup> indicated a singlet at 184.8 and 16.6 ppm, respectively. These results clearly indicated that the diamine prepared herein was consistent with the proposed structure.

#### 3.2. Polymer synthesis

As described in **Scheme 2**, the polyimides (**6a–6e**) were synthesized by conventional two-step procedure by the reaction of equal molar amounts of the diamine (**3**) with various aromatic dianhydrides (**4a–4e**) to form the poly(amic acid)s (PAAs) (**5a–5e**) and subsequent thermal cyclodehydration or chemical cyclodehydration. The inherent viscosities of the PAA precursors (**5a–5e**), measured by an Ubbelohde viscometer and their values were in the 0.87–1.58 g/dL range (**Table 1**). Furthermore, as shown in **Table 2**, these PI polymers had number-average molecular weights (*M<sub>n</sub>*) in the range of 28,700 to 33,700 g/mol with the polydispersity index in the 1.64–1.72 range. These characteristics clearly showed that these polyimides have relatively high molecular weights and good dispersion.

All of these PAAs could be thermally imidized at temperatures up to 300 °C under vacuum to produce flexible and



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

transparent polyimide films. Besides, the PAAs could also be chemically cyclodehydrated to the corresponding polyimides by treatment with a mixture of pyridine and acetic anhydride. The imidization process of polymers was verified by FTIR spectroscopy. The typical FTIR spectra of PAA (**5a**) and the polyimide (PI-**6a**) were shown in **Figure 3**. The FTIR spectrum of PAA-**5a** (**Figure 3a**) exhibited major absorption peaks at 1720, 1657, 1538 and 1250 cm<sup>-1</sup>, assigned to acid carbonyl, amide I, amide II and aryl ether group, respectively, along with characteristic absorption around 3250 cm<sup>-1</sup> for N–H and O–H groups, and the PI-**6a** obtained by thermal imidization, had the characteristic bands at 1770 (asymmetric C=O stretching) and 1730 cm<sup>-1</sup> (symmetric C=O stretching) of the imide group, as well as the C–N absorption band at 1373 cm<sup>-1</sup> (**Figure 3b**), with no absorption bands of 1657 and 1538 cm<sup>-1</sup>, which showed the high temperature imidization reaction was complete.

#### 3.3. Solubility

**Table 2** listed the solubility of the polymer samples, which were tested quantitatively in various organic solvents. On the whole, the resulting polyimides (**6a–6e**) prepared *via* chemical conversion method had better solubility compared with those obtained by the thermal procedure. Except for the polyimide (**6a**), the other polyimides obtained through chemical imidization were soluble in a wide range of organic solvents such as NMP, DMF, DMAc, Py and *m*-cresol at room temperature. Moreover, the polyimide (PI-**6e**) derived from 6FDA by both thermal and chemical imidization, is



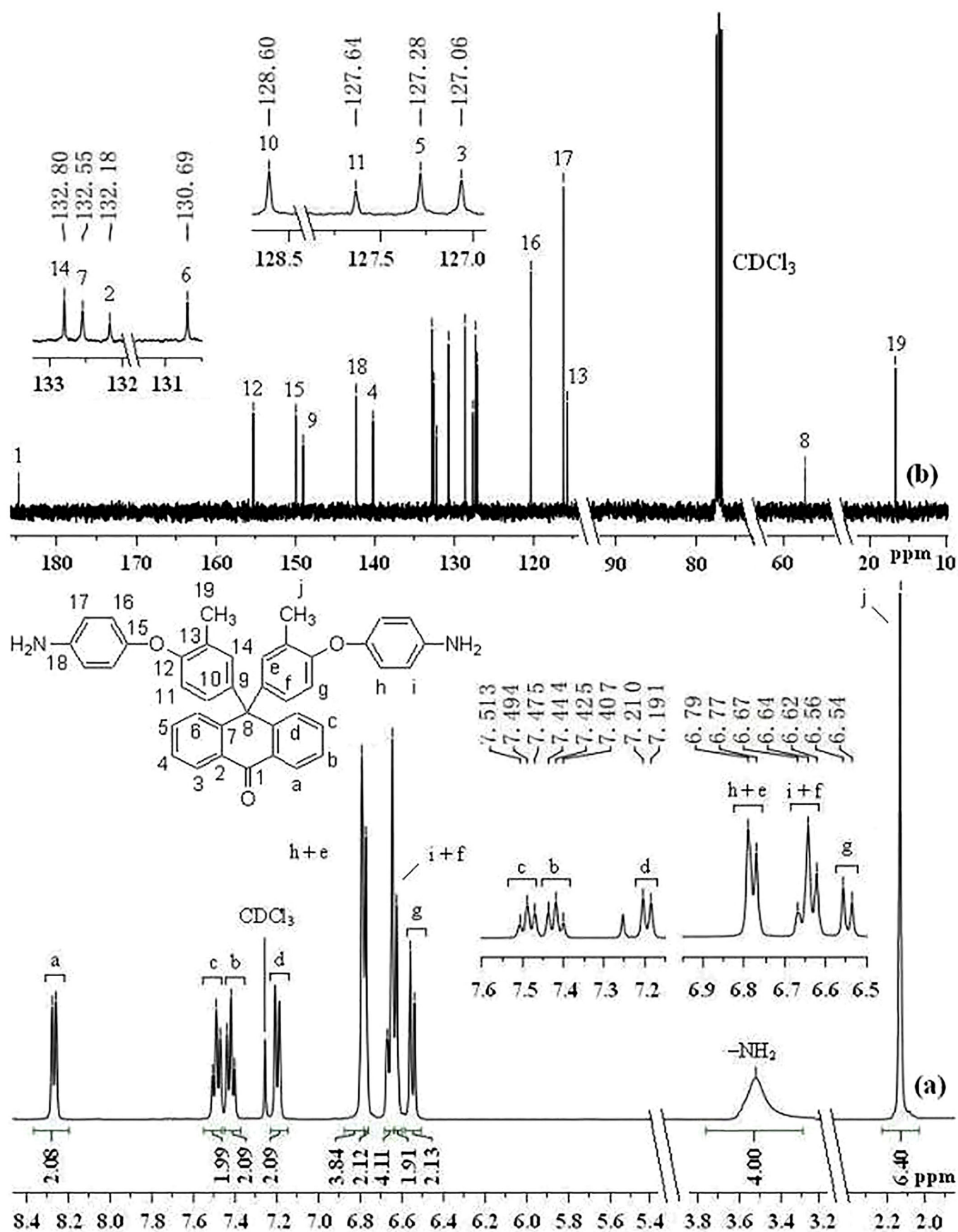
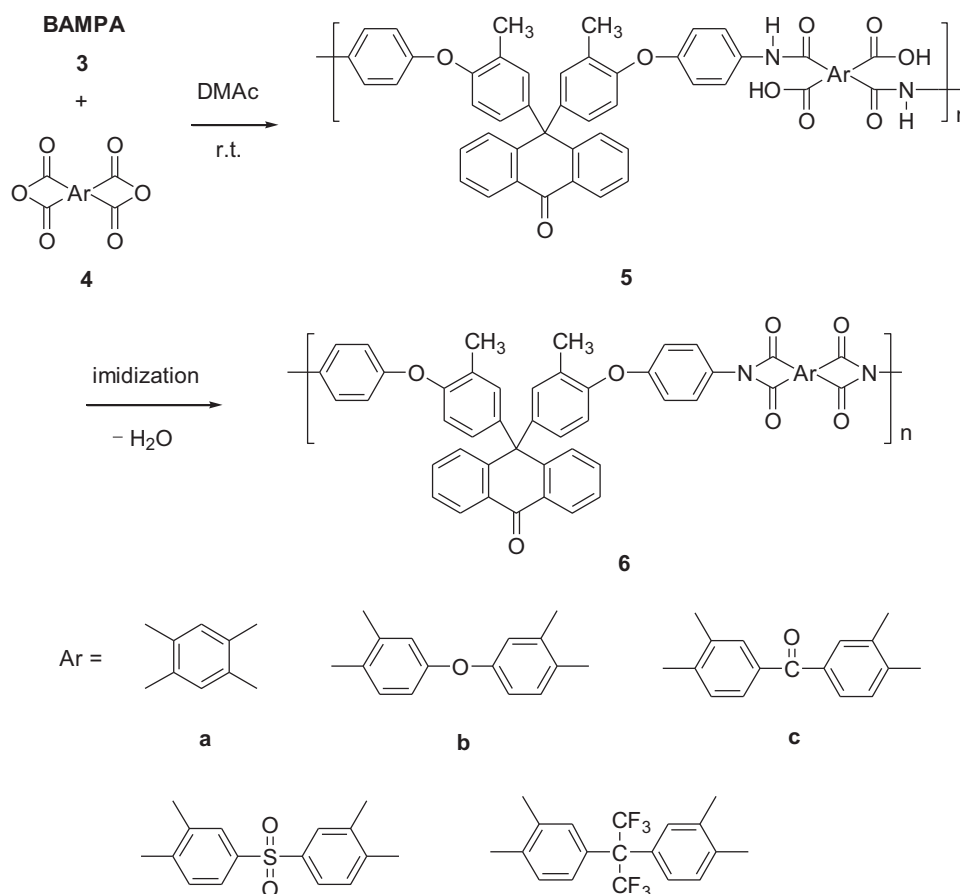


Figure 2.  $^1\text{H}$  NMR (a) and  $^{13}\text{C}$  NMR (b) spectra of the diamine (3).



**Scheme 2.** Structures of the polyimides (**6a–6e**) and polymerization route.

**Table 1.** Inherent viscosity of the PAAs and elemental analysis of Pls.

PAAs (5a–5e)		PIs (6a–6e)						
Code	$\eta_{\text{inh}}$ (dL/g) <sup>a</sup>	Code	$\eta_{\text{inh}}$ (dL/g) <sup>b</sup>	Formula (molecular weight)	Elemental analysis (%) <sup>c</sup>			
					C	H	N	
5a	1.45	6a	1.22	(C <sub>50</sub> H <sub>30</sub> N <sub>2</sub> O <sub>7</sub> ) <sub>n</sub> (770.80) <sub>n</sub>	Calcd.	77.91	3.92	3.63
					Found	77.05	4.19	3.82
					Found	(77.24)	(4.05)	(3.74)
5b	0.87	6b	0.77	(C <sub>56</sub> H <sub>34</sub> N <sub>2</sub> O <sub>8</sub> ) <sub>n</sub> (862.89) <sub>n</sub>	Calcd.	77.95	3.97	3.25
					Found	77.02	4.26	3.37
					Found	(77.56)	(4.13)	(3.29)
5c	1.58	6c	1.40	(C <sub>57</sub> H <sub>34</sub> N <sub>2</sub> O <sub>8</sub> ) <sub>n</sub> (874.91) <sub>n</sub>	Calcd.	78.25	3.92	3.20
					Found	77.12	4.25	3.33
					Found	(77.67)	(4.14)	(3.09)
5d	1.50	6d	1.27	(C <sub>56</sub> H <sub>34</sub> N <sub>2</sub> O <sub>9</sub> S) <sub>n</sub> (910.96) <sub>n</sub>	Calcd.	73.84	3.76	3.08
					Found	72.72	3.98	3.23
					Found	(73.13)	(3.88)	(3.26)
5e	1.31	6e	1.08	(C <sub>59</sub> H <sub>34</sub> F <sub>6</sub> N <sub>2</sub> O <sub>7</sub> ) <sub>n</sub> (996.92) <sub>n</sub>	Calcd.	71.08	3.44	2.81
					Found	70.01	3.58	2.97
					Found	(70.67)	(3.76)	(2.90)

<sup>a</sup>Measured at a concentration of 0.5 g/dL in DMAc at 30 °C.

<sup>b</sup>Measured at a concentration of 0.5 g/dL in NMP at 30 °C for the Pls by chemical imidization.

<sup>c</sup>Data in parentheses are for the Pls by chemical imidization.

soluble in most tested solvents at room temperature, which indicated the presence of hexafluoroisopropylidene units in its main chain could further enhance the solubility.

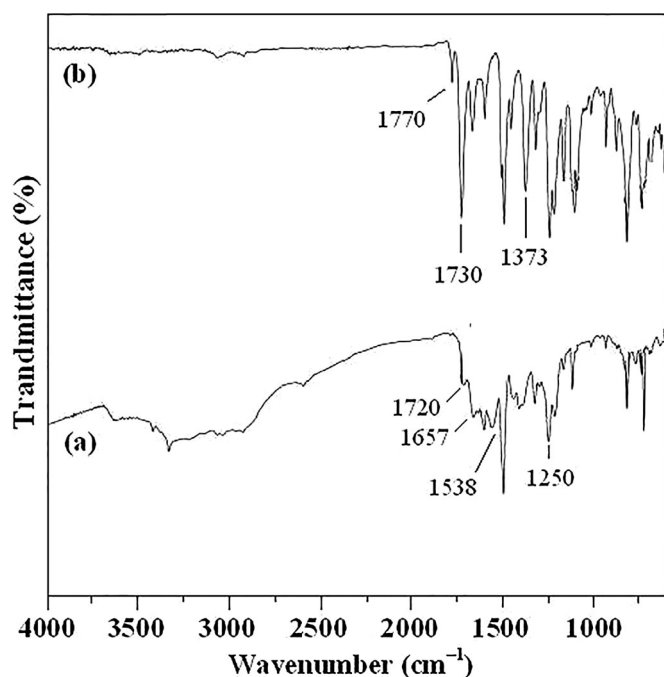
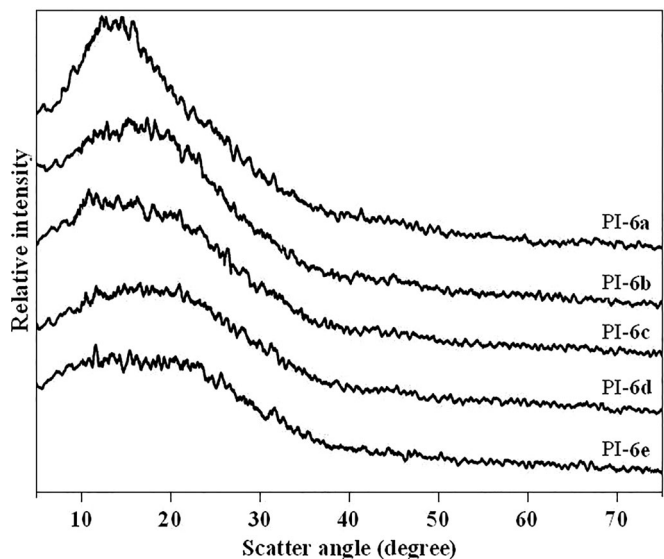
### 3.4. Crystallinity and tensile property

Wide-angle X-ray diffraction (WAXD) studies of the polymers show that all polyimides (**6a–6e**) exhibited amorphous

patterns (Figure 4), primarily because of the bulky pendant 9(10*H*)-anthrone groups. There is no doubt that the flexible ether and methyl groups certainly reduced the rigidity of the polymer chains to some extent. Generally, most of cardo polymers show amorphous structure under the influence of bulky side groups, which makes this kind of polymers have good solution processability.

**Table 2.** Molecular weight and solubility in various solvents of the polyimides.

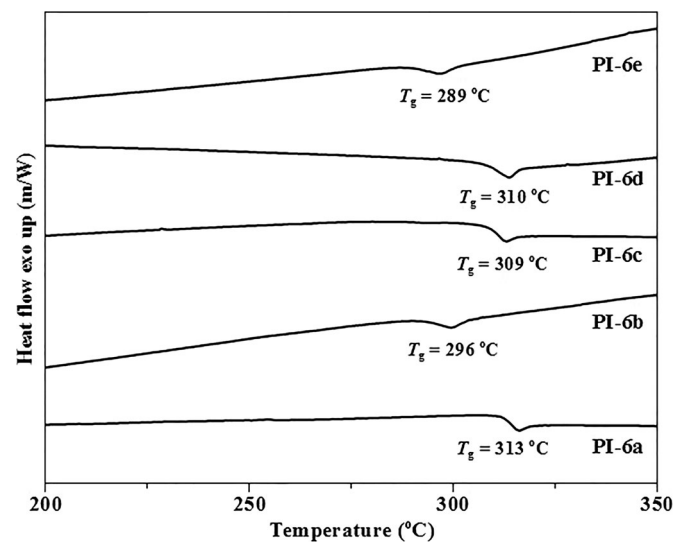
PIs	Molecular weights <sup>a</sup>			Solubility <sup>d</sup>							
	$M_w$	$M_n$	PDI <sup>b</sup>	NMP	DMAC	DMF	DMSO	Py	<i>m</i> -Cresol	THF	CHCl <sub>3</sub>
PI-6a	— <sup>c</sup>	— <sup>c</sup>	— <sup>c</sup>	+ - (+ +)	-- (- -)	-- (- -)	-- (- -)	-- (- -)	-- (+ +)	-- (- -)	-- (- -)
PI-6b	51,400	30,900	1.66	+ - (+ +)	-- (+ +)	-- (+ +)	-- (+ -)	-- (+ +)	-- (+ +)	-- (+ -)	-- (- -)
PI-6c	64,200	37,700	1.70	+ + (+ +)	+ - (+ +)	+ - (+ +)	-- (+ -)	+ - (+ +)	-- (+ +)	-- (+ -)	-- (- -)
PI-6d	59,800	36,500	1.64	+ + (+ +)	+ + (+ +)	+ + (+ +)	+ - (+ +)	+ + (+ +)	+ - (+ +)	-- (+ -)	-- (- -)
PI-6e	49,400	28,700	1.72	+ + (+ +)	+ + (+ +)	+ + (+ +)	+ + (+ +)	+ + (+ +)	+ + (+ +)	+ + (+ +)	+ - (+ -)

<sup>a</sup>Weight average molecular weights were obtained using DMF as an eluent and polystyrene as standard.<sup>b</sup>Polydispersity index (PDI) was obtained by  $M_w/M_n$ .<sup>c</sup>Polymer was insoluble in DMF.<sup>d</sup>Tested with 10 mg polymer sample in 1 mL solvent with stirring at room temperature. Data in parentheses are the solubility of the PIs by chemical imidization. + + = soluble; + - = partial soluble; -- = insoluble. NMP, *N*-methyl-2-pyrrolidone; DMAC, *N,N*-dimethylacetamide; DMF, *N,N*-dimethylformamide; DMSO, dimethylsulfoxide; THF, tetrahydrofuran; Py, Pyridine.**Figure 3.** FTIR spectra of the PAA-5a (a) and PI-6a (b).**Figure 4.** WAXD curves of the polyimides (6a–6e).**Table 3.** Tensile properties of the polyimide films.

PIs	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (GPa)
PI-6a	93.47	8.74	1.98
PI-6b	119.74	12.33	2.38
PI-6c	80.22	7.58	2.16
PI-6d	76.43	6.93	2.07
PI-6e	86.53	11.16	1.91

**Table 4.** Thermal behavior data of the polyimides.<sup>a</sup>

PIs	$T_g$ (°C) <sup>b</sup>	$T_{d10}$ (°C) <sup>c</sup>	$R_w$ (%) <sup>d</sup>	$T_m$ (°C) <sup>e</sup>
PI-6a	313 (312)	484 (488)	61 (62)	560
PI-6b	296 (298)	495 (495)	60 (60)	566
PI-6c	309 (310)	520 (524)	63 (60)	584
PI-6d	310 (308)	511 (513)	55 (55)	575
PI-6e	289 (290)	513 (512)	58 (59)	580

<sup>a</sup>Data in parentheses are the thermal property of the PIs by chemical imidization.<sup>b</sup>Glass-transition temperature from the second heating trace of DSC measurements.<sup>c</sup>The decomposition temperature at a 10% weight loss obtained by TGA in nitrogen.<sup>d</sup>Residual weight percentage at 800 °C obtained by TGA in nitrogen.<sup>e</sup>Temperature at the maximum-rate degradation obtained by DTG in nitrogen.**Figure 5.** DSC curves of the polyimides (6a–6e).



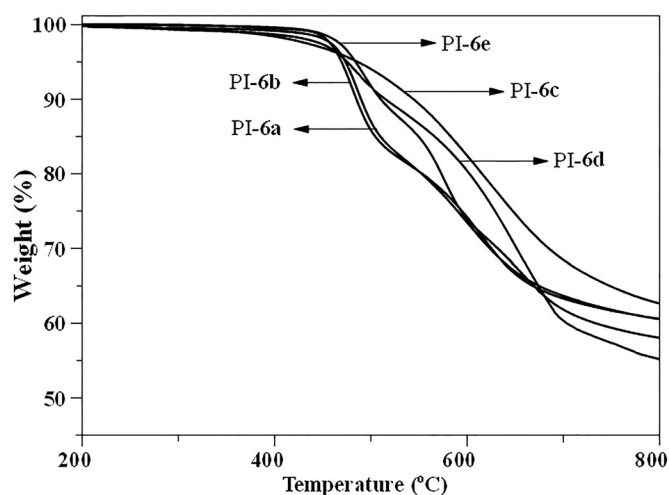
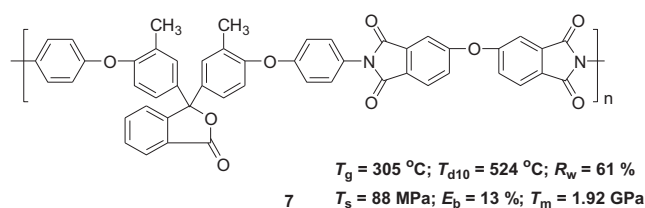


Figure 6. TGA curves of the polyimides (6a–6e).



Scheme 3. The structure of the similar cardo polyimide (7).

Table 3 gave the tensile properties of the polyimide films (6a–6e) prepared by the thermal conversion method, which had tensile strength of 76.43–119.74 MPa, elongation at break of 6.93–12.33%, and tensile modulus of 1.91–2.38 GPa.

### 3.5. Thermal property

Differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and differential thermal gravity (DTG) were used to investigate the thermal properties of the polyimides (6a–6e), and the thermal behavior data of all the polymers are summarized in Table 4. DSC and TGA curves of these polyimide samples were displayed in Figures 5 and 6, respectively. As shown in Table 4, the  $T_g$ s of these polyimides were in the range of 289–313 °C. As expected, PI-6a obtained from PMDA (4a) had the highest  $T_g$  (313 °C) as a result of its most rigid polymer backbone. In addition, the relatively high  $T_g$  (310 °C) of PI-6d could be due to the polar sulfonyl group incorporated in the main chain.

All the polyimides showed a similar pattern of decomposition (Figure 6) with no significant weight loss below 420 °C under nitrogen. Seen from Table 4, the 10% weight loss temperatures in nitrogen were in the range of 484–524 °C, and their char yields at 800 °C were above 55%, implying that the present polyimides possess good thermal stability. Besides, the temperatures at the maximum-rate degradation of these polyimides were in the range of 560–584 °C, obtained from DTG analysis in nitrogen. On the other hand, it should be noted that almost all polyimides seemed to have two-step degradation pattern. The first weight loss might be closely associated with the thermal degradation of the methyl groups.

In comparison, the thermal and tensile properties of the present corresponding polyimide (PI-6b) are comparable to those of the analogous polyimide (7) (Scheme 3).<sup>[19]</sup>

## 4. Conclusions

This study successfully prepared the new diamine, 10,10-bis[4-(4-aminophenoxy)-3-methylphenyl]-9(10H)-anthrone (BAMPA) containing bulky 9(10H)-anthrone units, methyl and flexible ether groups using anthrone as starting material. Additionally, a series of new polyimides with moderate to high inherent viscosities, derived from BAMPA exhibit good mechanical properties, thermal stability and solution processability. These BAMPA-based polyimides can be considered as new processable high-performance polymer materials, which are expected to have potential applications in aerospace, liquid crystal display, gas separation, microelectronic devices and other fields. Besides, Methyl can be converted into some functional groups such as benzyl, aldehyde and carboxyl groups. Thus, the current polyimides are expected to become functional polymers with potential application values.

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