Synthesis and Properties of Novel Aromatic Polyamides with Xanthene Cardo Groups

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ABSTRACT: Two novel monomers, 9,9-bis[4-(4-carboxyphenoxy)phenyl]xanthene (BCAPX) and 9,9-bis[4-(4-aminophenoxy)phenyl]xanthene (BAPX) were prepared in two main steps starting from nucleophilic substitution of 9,9-bis(4-hydroxyphenyl)xanthene (BHPX) with *p*-fluorobenzonitrile and *p*-chloronitrobenzene, respectively. Using triphenyl phosphite and pyridine as condensing agents, two series of polyamides containing xanthene cardo groups with the inherent viscosities (0.82–1.32 dL/g) were prepared by polycondensation from BCAPX with various aromatic diamines or from BAPX with various aromatic dicarboxylic acids in an *N*-methyl-2-pyrrolidone (NMP) solution containing dissolved calcium chloride, respectively. All new polyamides were amorphous and readily soluble in various polar solvents such as *N,N*-dimethylformamide (DMF), NMP, *N,N*-dimethylacetamide (DMAc) and pyridine. These polymers showed relatively high glass transition temperatures between 264 and 308°C, decomposition temperatures at 10% weight loss ranging from 502 to 540°C and 488 to 515°C in nitrogen and air, respectively, and char yields at 800°C in nitrogen higher than 56%. Transparent, flexible, and tough films of these polymers cast from DMAc solutions exhibited tensile strengths ranging from 86 to 109 MPa, elongations at break from 13 to 22%, and initial moduli from 2.15 to 2.63 GPa. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 116: 1650–1659, 2010

Key words: polyamide; xanthene cardo unit; 9,9-bis[4-(4-carboxyphenoxy)phenyl]xanthene; 9,9-bis[4-(4-aminophenoxy)phenyl]xanthene

INTRODUCTION

Aromatic polyamides such as poly (*p*-phenylene terethphalamide) and poly (*m*-phenylene isophthalamide) constantly attract much interest because of their high-temperature stability, excellent mechanical strength, and good chemical resistance that qualify them as high-performance polymeric materials.[1,2] However, these materials suffer often poor processabilitiy due to their high melting or softening temperatures and limited solubility in most of organic solvents partly because of the strong interchain interaction, thus limiting their applications. To overcome these limitations, many efforts have been made with the aim of making structural modifications of the polymer backbone, such as the introduction of ether linkages,[3,4] substituted methylene linkages[5,6] as well as asymmetrical structures[7–12] into the aromatic polymer main chains and the incorporation of bulky substituents[13–16] within the parent chain. Another successful approach for improving the processability of aromatic polyamide without an extreme loss of their outstanding properties is to incorporate cardo groups into the polymer backbone. The introduction of cardo groups along the polymer backbone has been shown to impart greater solubility, enhanced rigidity, and better mechanical and thermal properties.[17] It has been reported that the presence of cardo groups such as fluorene,[18,19] phthalide,[20] phthalimidine,[21,22] cyclododecylidene,[23] adamantine,[24] tricyclo [5.2.1.0^{2,6}]decane,[25] norbornane[26] and *tert*-butylcyclohexylidene[27] groups into the backbone of polyamides yields polymers with enhanced solubility, processability, and good thermal stability. Although many excellent polyamides are known and commercially available, new polyamides are continuing to appear as researchers continue to conduct fundamental studies on chemical structure/property relationships. In previous study, polymers containing xanthene cardo groups in the polymeric chain such as poly (aryl ether)s[28,29] and poly (aryl ester)s[30] have been prepared and characterized. However, to our knowledge, polyamides with xanthene cardo groups have not been reported. Herein, we wish to describe the synthesis and characterization of a series of novel polyamides containing xanthene cardo group in the main chain. The solubility, crystallinity, and thermal and mechanical properties of the polymers were also investigated.

EXPERIMENTAL

Materials

Xanthone, phenol, *p*-fluorobenzonitrile, and *p*-chloronitrobenzene were used as received. 9,9-Bis(4-hydroxyphenyl)xanthene (BHPX) was synthesized by reaction of xanthone with thionyl chloride, followed by treatment with phenol in refluxing xylene according to our recent method,[31] and then recrystallized from toluene; mp 239–240°C (lit.[30] 241°C). Reagent grade aromatic diamines (Aldrich Co.) such as *p*-phenylenediamine (PPD) (**4a**), *m*-phenylenediamine (MPD) (**4b**) and 4,4′-oxydianiline (ODA) (**4d**) were purified by sublimation; 4,4′-methylenedianiline (MDA) (**4f**) was crystallized twice from benzene. Benzidine (**4c**) and 1,4-bis(4-aminophenoxy)benzene (**4e**) were recrystallized from ethanol. Aromatic dicarboxylic acids (Aldrich Co.) such as terephthalic acid (**5a**), isophthalic acid (**5b**), 4,4′-oxydibenzoic acid (**5c**) and 4,4′-biphenyldicarboxylic acid (**5d**) were used as received. Anhydrous potassium carbonate (Beijing Chemical Reagent Co., China) was dried in vacuum at 100°C before use. Anhydrous calcium chloride ($CaCl_2$) was dried under vacuum at 200°C for 10 h. LiCl was dried for 16 h at 180°C under vacuum. Triphenyl phosphite (TPP) was purified by fractional distillation under reduced pressure. Pyridine (Py) was refluxed in an inert atmosphere in the presence of KOH for 6 h, distilled and stored over 4 Å molecular sieves. *N*-Methyl-2-pyrrolidone (NMP) was distilled over calcium hydride under reduced pressure and stored over 4 Å molecular sieves.

Monomer synthesis

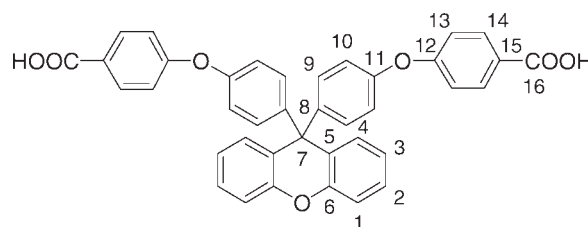9,9-Bis[4-(4-cyanophenoxy)phenyl]xanthene (BCYPX) (2a)

In a 250-mL round-bottom flask equipped with a Dean–Stark trap and a condenser, BHPX (**1**) (36.6 g, 0.1 mol) was dissolved in a mixture of *N,N*-dimethylformamide (DMF) (200 mL) and toluene (50 mL). Anhydrous potassium carbonate (27.6 g, 0.2 mol) was added to this solution. The suspension solution was heated to reflux, and water was removed by azeotropic distillation with toluene. After the water was completely removed, the residual toluene was distilled out from the system. Then the reaction mixture was cooled to about 60°C, and *p*-fluorobenzonitrile (24.3 g, 0.2 mol) was added. After refluxing at 150°C for 6 h, the solution was allowed to cool and poured into 500 mL of water. The precipitated white powder was collected by filtration, thoroughly washed with water, and dried. The crude product was purified by recrystallization from acetonitrile to give a white fine granular crystal; yield, 47.2 g (83 %); m.p. 219–220 °C. FTIR (KBr):ν_{max} = 2227 (CN

stretch) and 1251 cm^{-1} (C—O—C stretch). ^{1}H NMR ($CDCl_3$): δ = 7.60 (d, *J* = 8.8 Hz, 4 H), 7.32 (t, *J* = 8.0 Hz, 2 H), 7.19 (d, *J* = 8.0 Hz, 2 H), 7.09 (t, *J* = 8.0 Hz, 2 H), 7.04–7.02 (m, 8 H), 6.96–6.93 (m, 6 H). ^{13}C NMR ($CDCl_3$): δ = 161.18 (C^{12}), 153.53 (C^6), 152.43 (C^{11}), 142.33 (C^8), 134.20 (C^{14}), 131.74 (C^9), 129.87 (C^5), 129.77 (C^2), 128.34 (C^4), 123.18 (C^3), 119.54 (C^{10}), 118.84 (C^{16}, CN), 118.23 (C^{13}), 116.75 (C^1), 106.09 (C^{15}), 53.54 (C^7). Elem. Anal. Calcd for $C_{39}H_{24}N_2O_3$ (568.63 g/mol): C, 82.38 %; H, 4.25 %, N, 4.93%. Found: C, 82.15 %; H, 4.35 %, N, 4.85%.
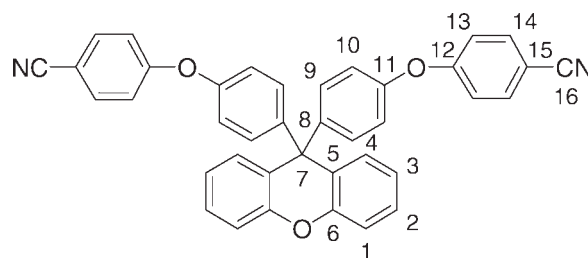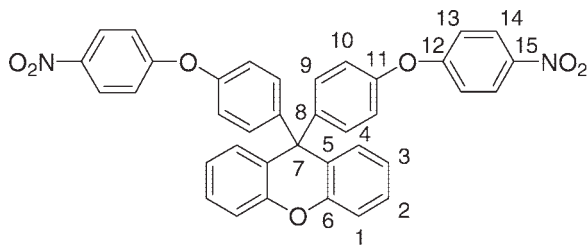

9,9-Bis[4-(4-carboxyphenoxy)phenyl]xanthene (BCAPX) (3a)

Xanthene-dinitrile (**2a**) (25.6 g, 0.045 mol), potassium hydroxide (51 g, 0.45 mol), ethanol (150 mL), and water (150 mL) were introduced into a 500-mL flask, and the suspension was refluxed for 2 days to form a clear solution. The resulting clear solution was filtered while hot to remove any possible impurities. After cooling to room temperature, the pH value of the filtrate was adjusted by concentrated hydrochloric acid to 2–3. The white precipitate formed was collected by filtration, washed repeatedly with water, and dried under vacuum at 150°C for 5 h; yield, 21.8 g (80 %); m.p. 247–249°C. FTIR (KBr):ν_{max} = 2500–3450 (H-bonded O—H stretch), 1681 (C=O stretch), and 1238 cm^{-1} (C—O—C stretch). ^{1}H NMR (DMSO-d_6): δ = 12.08 (s, 2 H), 7.91 (dd, *J* = 8.4, 8.8 Hz, 4 H), 7.36 (t, *J* = 7.6 Hz, 2 H), 7.25 (d, *J* = 8.0 Hz, 2 H), 7.17 (t, *J* = 7.6 Hz, 2 H), 7.08 (d, *J* = 8.8 Hz, 8 H), 6.98–6.95 (m, 6 H). ^{13}C NMR ($CDCl_3$): δ = 171.36 (C^{16}, CO), 162.18 (C^{12}), 154.26 (C^6), 152.51 (C^{11}), 141.84 (C^8), 132.44 (C^{14}), 131.57 (C^9), 129.94 (C^{15}), 129.91 (C^5), 128.21 (C^2), 123.79 (C^4), 123.08 (C^3), 119.23 (C^{10}), 117.69 (C^{13}), 116.68 (C^1), 53.52 (C^7). Elem. Anal. Calcd for $C_{39}H_{26}O_7$ (606.63 g/mol): C, 77.22 %; H, 4.32%. Found: C, 77.03 %; H, 4.41%.

9,9-Bis[4-(4-nitrophenoxy)phenyl]xanthene (BNPX) (2b)

BHPX (**1**) (36.6 g, 0.1 mol) and *p*-chloronitrobenzene (31.5 g, 0.2 mol) were dissolved in 150 mL of DMF. Anhydrous K_2CO_3 (27.3 g, 0.2 mol) was added to this solution, and the suspension was then refluxed at 160°C for 8 h. After cooling to room temperature, the mixture was poured into 500 mL of water to precipitate a yellow solid that was collected by filtration, washed with hot water, and dried. The crude product was purified by recrystallization from DMF/methanol; yield, 49.3 g (81 %); m.p. 263–264°C. FTIR (KBr):ν_{max} = 1515, 1344 cm^{-1} (N=O stretch), 1248 cm^{-1} (C—O—C stretch). ^1H NMR (CDCl$_3$): δ = 8.19 (d, J = 8.6 Hz, 4 H), 7.31 (t, J = 8.0 Hz, 2 H), 7.20 (d, J = 8.0 Hz, 2 H), 7.09 (t, J = 7.6 Hz, 2 H), 7.07–7.03 (m, 8 H), 6.99–6.94 (m, 6 H). ^{13}C NMR (CDCl$_3$): δ = 162.38 (C^{12}), 152.67 (C^6), 151.48 (C^{11}), 148.50 (C^8), 142.25 (C^8), 141.92 (C^{15}), 131.22 (C^8), 129.74 (C^5), 129.45 (C^4), 128.31 (C^2), 125.94 (C^{14}), 123.12 (C^3), 119.97 (C^{10}), 117.25 (C^{13}), 116.70 (C^1), 53.51 (C^7). Elem. Anal. Calcd for $C_{37}H_{24}N_2O_7$ (608.61 g/mol): C, 73.02 %; H, 3.97 %; N, 4.60%. Found: C, 73.12 %; H, 3.90 %; N, 4.70%.

9,9-Bis[4-(4-aminophenoxy)phenyl]xanthene (BAPX) (3b):

A mixture of dinitro compound (**2b**) (29 g, 0.05 mol), hydrazine hydrate (27 g) and 10% Pd/C catalyst (0.1 g) in ethanol (200 mL) was refluxed overnight. The resulting solution was filtered hot to remove the catalyst. The filtrate was cooled to room temperature and precipitated into water. The product was collected by filtration and dried; yield, 23.3 g (85 %); m.p. 209–211°C (by DSC). FTIR (KBr):ν_{max} = 3370, 3223 cm^{-1} (N—H stretch), 1172 cm^{-1} (C—O—C stretch). ^1H NMR (CDCl$_3$): δ = 7.25 (t, J = 7.6 Hz, 2 H), 7.13 (d, J = 8.0 Hz, 2 H), 7.02 (t, J = 8.8 Hz, 2 H), 6.92 (d, J = 8.0 Hz, 2 H), 6.87–6.81 (m, 8 H), 6.77 (dd, J = 8.0 Hz, 4 H), 6.65 (dd, J = 8.0 Hz, 4 H), 3.53 (br s, 4 H). ^{13}C NMR (CDCl$_3$): δ = 157.47 (C^6), 152.62 (C^{11}), 148.26 (C^{12}), 142.78 (C^{15}), 139.38 (C^8), 131.07 (C^9), 130.54 (C^5), 130.03 (C^2), 127.80 (C^4), 122.82 (C^3), 121.32 (C^{13}), 116.41 (C^1), 116.20 (C^{14}), 116.14 (C^{10}), 53.20 (C^7). Elem. Anal. Calcd for $C_{37}H_{28}N_2O_3$ (548.64 g/mol): C, 81.00 %; H, 5.14 %; N, 5.11%. Found: C, C, 81.14 %; H, 5.23 %; N, 5.20%.
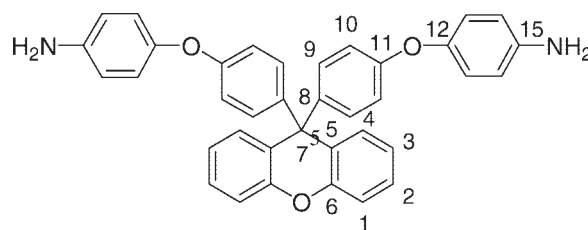
Polymer synthesis

A typical synthesis for polyamide **6d** is as follows. A mixture of 0.7008 g (1.25 mmol) of diacid **3a**, 0.2503 g (1.25 mmol) of 4,4′-oxydianiline (**4d**), 0.3 g of calcium chloride, 0.8 mL of triphenyl phosphite, 0.8 mL of pyridine, and 4 mL of NMP was heated with stirring at 120°C for 3 h. The obtained viscous polymer solution was poured slowly into 300 mL of stirring methanol to precipitate a white fiberlike product, which was isolated by filtration, thoroughly washed first with methanol and then with boiling water, and dried at 150°C under vacuum. The yield was almost quantitative. The inherent viscosity of the polyamide (**6d**) was 1.15 dL/g, as measured at a concentration of 0.5 g/dL in DMAc at 30°C. The IR spectrum exhibited absorptions at 3500 (N—H stretch), 1651 (C=O stretch), and 1243 cm^{-1} (C—O—C stretch).

The other polyamides were synthesized analogously.

Measurements

^1H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on Bruker Avance 400 MHz spectrometer in dimethyl sulfoxide-d_6 (DMSO-d_6) or chloroform (CDCl$_3$). FT-IR spectra of the monomer and polymers in KBr pellets were determined on a Perkin-Elmer SP One FTIR spectrophotometer. Microanalyses were performed with a Carlo Erba 1106 Elemental Analyzer. Melting points were determined on X_4 melting point apparatus and are uncorrected, unless otherwise specified. The glass-transition temperatures (Tg's) were performed on a Perkin-Elmer DSC-7 instrument at a heating rate of 20°C/min under nitrogen protection. The second scan was immediately initiated after the sample was cooled to room temperature. The T_g 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. The thermal stability of the polymers from 50 to 800°C was determined with a Seiko SSC-5200 thermogravimetric analysis (TGA) at a heating rate of 10°C/min under a protective nitrogen atmosphere (120 mL/min) or in air. Wide-angle X-ray diffraction patterns were recorded at room temperature (ca.25°C) on power with a Rigaku Geiger Flex D-Max III x-ray diffractometer, using Ni-filtered CuK$_\alpha$ radiation (operating at 40 kV and 15 mA); the scanning rate was 2°/min
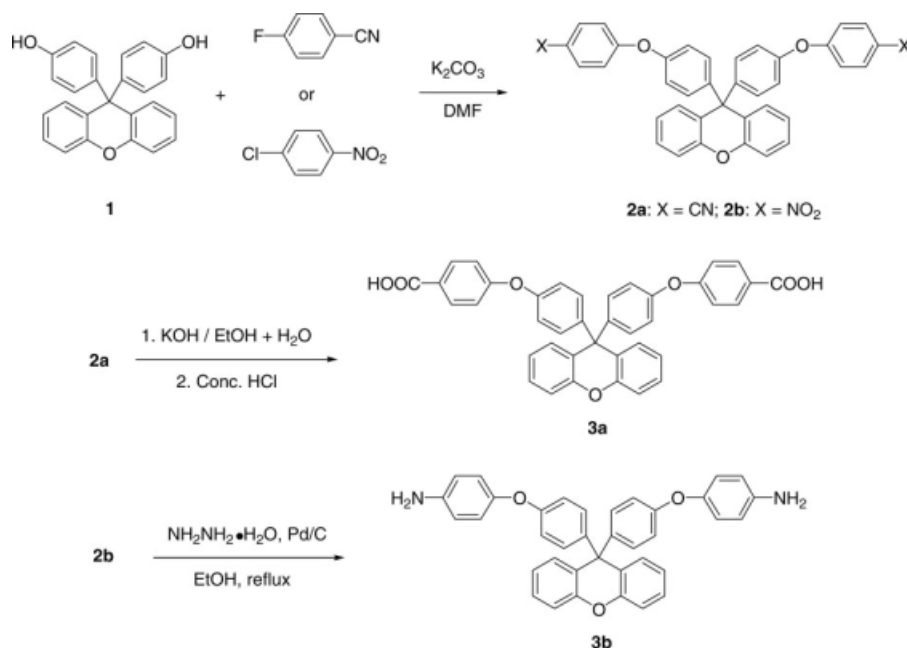
Scheme 1 Synthesis of the diacid **3a** and diamine **3b**.

over a range of 2 Θ = 2–40°). The mechanical properties were measured on an Instron 1122 testing instrument with 120 × 5 mm^2 specimens in accordance with GB1040-79 at a drawing rate of 50 mm/min. The inherent viscosities were measured at 0.5g/dL concentration in DMAc with an Ubbelohde viscometer at 30°C, in which the polyamides were pretreated by drying in oven at 120°C for 1 h to remove the adsorbed moisture.

RESULTS AND DISCUSSION

Monomer synthesis

Previously, 9,9-bis(4-hydroxyphenyl)xanthene (BHPX) (**1**) was synthesized from 9,9-dichloroxanthene with excess of phenol in the presence of 3-mercaptopropionic acid,[30] but the yield of BHPX was low (14 %). In our recent study, 82% yield of BHPX was obtained by reaction of xanthone with thionyl chloride, affording 9,9-dichloroxanthene, followed by treatment with phenol in refluxing xylene in a one-pot, two-step synthetic procedure.[31]

9,9′-Bis[4-(4-carboxyphenoxy)phenyl]xanthene (**3a**) and 9,9-bis[4-(4-aminophenoxy)phenyl]xanthene (**3b**) were prepared in two steps according to Scheme 1. Intermediate compounds 9,9-bis[4-(4-cyanophenoxy)phenyl]xanthene (**2a**) and 9,9-bis[4-(4-nitrophenoxy)phenyl]xanthene (**2b**) were synthesized by nucleophilic aromatic halogen displacement of p-fluorobenzonitrile and p-chloronitrobenzene, respectively, with BHPX (**1**) in the presence of potassium carbonate in DMF. The dinitrile **2a** was then readily

converted into dicarboxylic acid **3a** by alkaline hydrolysis. The diamine **3b** was obtained by catalytic hydrogenation of the dinitro compound **2b** using hydrazine hydrate and Pd/C catalyst in refluxing ethanol. All the intermediate and monomer structures were confirmed by FT-IR, NMR, and elemental analysis.

Figure 1 presents the FTIR spectra of dinitrile **2a** and diacid **3a**. Characteristic bands for CN stretch at 2227 and C—O—C at 1251 cm^{-1} are consistent with structure **2a**. After hydrolysis, the CN peak disappeared and typical bands for the carboxyl groups
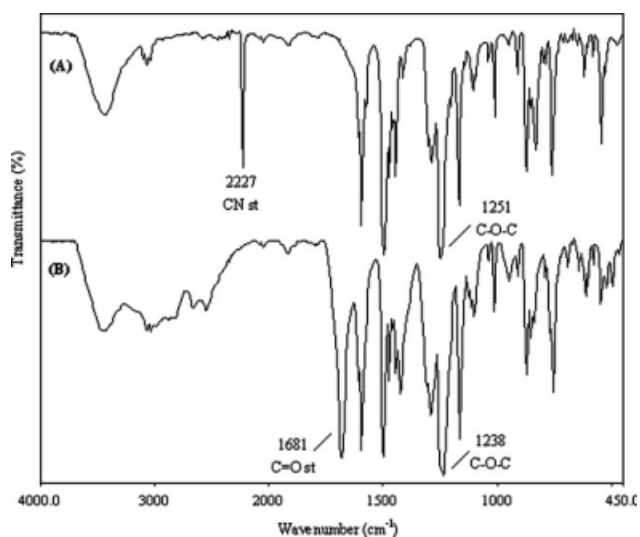

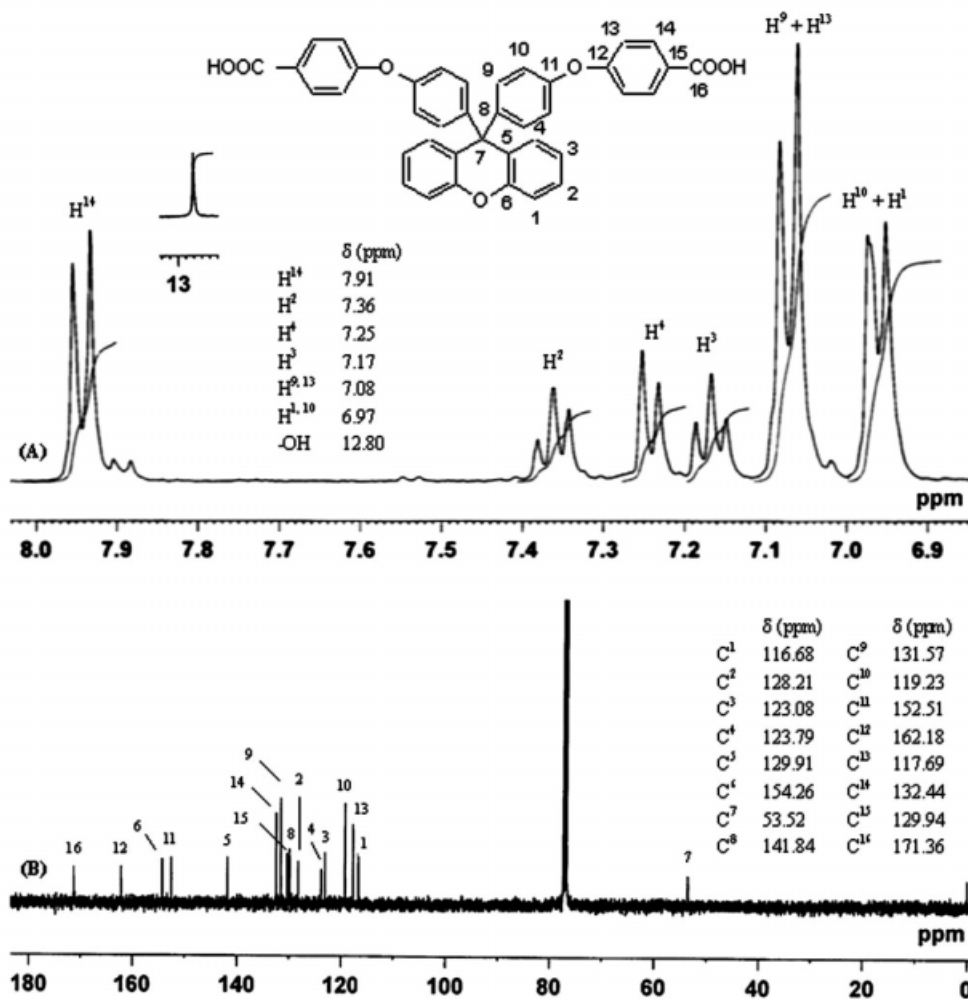**Figure 1** IR spectra of of dinitrile **2a** (A) and diacid **3a** (B).

Figure 2 (A) ^{1}H-NMR (DMSO-d_6) and (B) ^{13}C-NMR (CDCl$_3$) spectra of dicarboxylic acid (**3a**).

were observed around 1681 (C=O stretch), C—O—C at 1238 cm^{-1} and 2500–3450 cm^{-1} (hydrogen-bonded O—H). When **2b** is reduced to **3b**, the FTIR spectra show that the absorption peaks of nitro groups in **2b** (1515 and 1344 cm^{-1}) disappeared, and the absorption peaks of amino groups in **3b** (3370 and 3223 cm^{-1}) appeared suddenly.

Figure 2 illustrates the ^{1}H-NMR and ^{13}C-NMR spectra of dicarboxylic acid **3a** in DMSO-d_6 and CDCl$_3$ solution, respectively. Assignments of peaks for both spectra are shown. In the ^{1}H-NMR spectrum, the aromatic protons (H^{14}) *ortho* to the carboxyl groups and those (H^2, H^3, and H^4) on the xanthene unit were clearly distinguished, whereas the aromatic protons (H^9 and H^{13}) *ortho* to the ether groups, those (H^{10}) *ortho* to the xanthene unit, and those (H^1) on the xanthene unit were overlapped. However, all carbon nuclei in diacid **3a** gave well-separated peaks in the ^{13}C-NMR spectrum. The resonance of carbonyl carbon occurred at the farthest downfield of 171.36 ppm.

Figure 3 shows the ^{1}H-NMR and ^{13}C-NMR spectra of diamine **3b** in CDCl$_3$ solution and the assignments to all carbons and protons. All expected absorptions are observed. In the ^{1}H-NMR spectrum, the absorption signals of aromatic protons appear in the range of δ 6.65–7.25 ppm, and all the aromatic protons except for those (H^9 and H^{13}) were clearly distinguished. The resonance at 3.53 ppm is due to the amino protons. Furthermore, in the ^{13}C-NMR spectrum, the C^{13} and C^{14} carbons are partially overlapped, whereas the other carbon nuclei show well-separated peaks.

Polymer synthesis

Two series of aromatic polyamides with xanthene cardo groups, **6a–6f** and **7a–7d**, were prepared from the diacid **3a** with various aromatic diamines **4a–4f** and from the diamine **3b** with various commercially available dicarboxylic acids **5a–5d** (Scheme 2) according to the procedure developed by Yamazaki et al.[32]
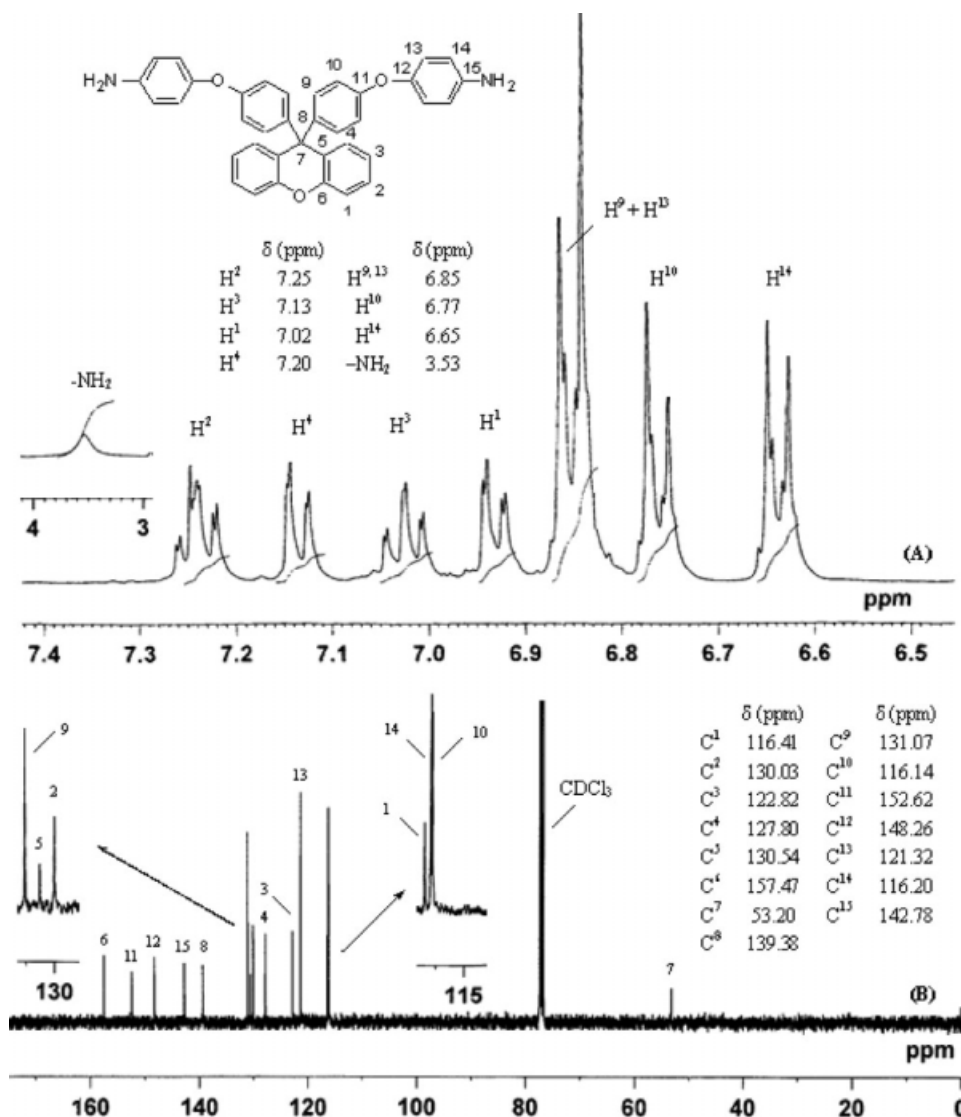
Figure 3 (A) ^{1}H-NMR and (B) ^{13}C-NMR spectra of diamine **3b** in CDCl$_3$ solution.

All polymerizations proceeded homogeneously throughout the reaction, and highly viscous solutions were obtained. The polyamides with white colors were isolated in good yields (95–97 wt %). The physical properties and elemental analysis of the xanthene-containing polyamides were listed in Table I. As shown in Table I, these obtained polyamides exhibited high inherent viscosity of 0.82 to 1.32 dL/g, which was high enough to obtain flexible and tough polymer film by casting from their DMAc solutions. The elemental analysis values of the polyamides are also listed in Table I. In all cases the carbon values were found to be lower than the calculated ones for the proposed structures. This can probably be explained by the high char yields of aromatic polyamides. On the other hand, moisture absorption could also give rise to slight differences in the values of the elemental analyses.

Structural features of these polyamides were conformed by FTIR and NMR spectroscopy. The FTIR spectra of these polyamides exhibited the characteristic absorptions of polyamides at 3300–3400 cm^{-1} (N—H stretching), 1650–1670 cm^{-1} (C=O stretching) and 1500–1550 cm^{-1} (combined N—H bending and C—N stretching), with strong absorptions of aryl ether group stretching in the region of 1230–1240 cm^{-1}. The only structure difference between polyamides **6a–6f** and **7a–7d** is the orientation of the amide groups. Figure 4 shows a typical ^{1}H-NMR and ^{13}C NMR spectra for the polyamide **7a**. Assignments of each carbon and proton are also given in the figures, and these spectra are in good agreement with the proposed structure. The resonance peaks appearing in the region of 10.42 ppm in the ^{1}H-NMR spectrum also support the formation of amide linkages. The results further
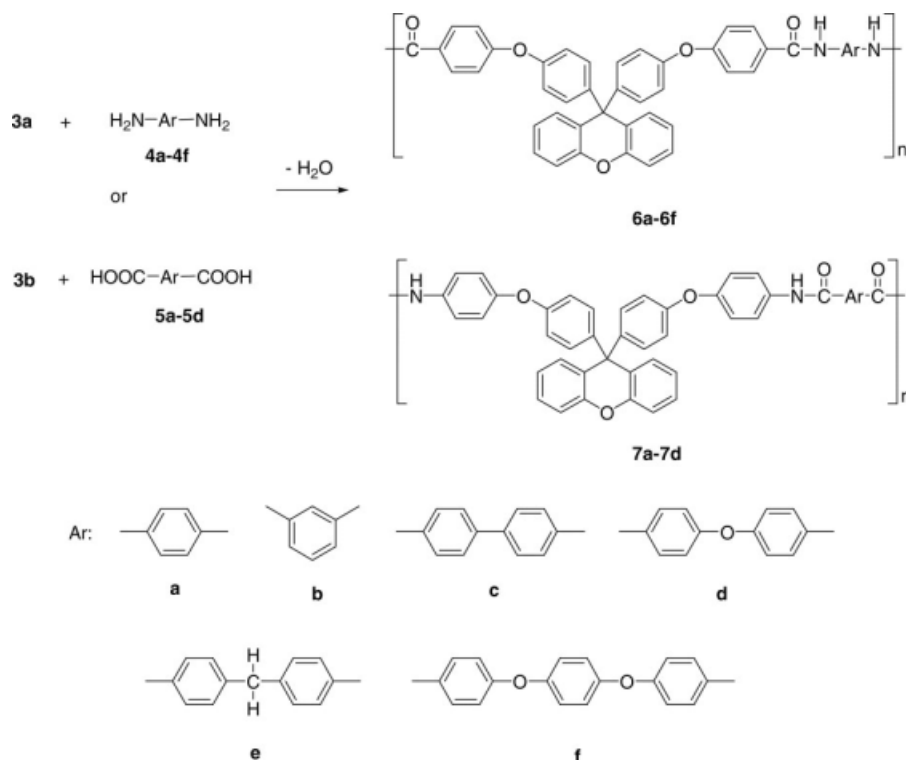
Scheme 2 Synthesis of polyamides **6a–6f** and **7a–7d**.

demonstrated that the polyamides containing xanthene units in the main linker have the expected chemical structures.

Thermal properties

The thermal behavior of these polymers evaluated by TG and DSC is summarized in Table II. Polyamides **6a–6f** and **7a–7d** showed the glass transition temperature (T_g) values in the range of 264–302°C and 271–308°C, respectively, by DSC. The T_g values generally decreased with the decreasing order of segmental flexibility of the diamine moiety. It should be pointed out that the polyamide **6c** and **7c** exhibited the higher T_g values (302 and 308°C, respectively) because of the effect of the rigid biphenylene polymer backbone. When the two sets of isomeric polyamides are compared, polyamides **6a–6d** displayed a comparable T_g with analogous **7a–7d** by means of DSC, indicating that constitutional isomerism of the recurring unit did not affect significantly the polymer rigidity.

The TG curves for these polymers, typical of which are shown in Figure 5, indicated that all of

TABLE I
Yields, Inherent Viscosities and Elemental Analysis of Polyamides

Polymer Code	Yield (%)	η_{inh} (dL/g)[a]	Formula	C (%) Calcd	C (%) Found	H (%) Calcd	H (%) Found	N (%) Calcd	N (%) Found
6a	96	1.05	$(C_{45}H_{26}N_2O_5)_n$	80.11	78.98	3.88	4.03	4.15	4.00
6b	95	1.01	$(C_{45}H_{26}N_2O_5)_n$	80.11	79.01	3.88	4.06	4.15	3.95
6c	97	1.17	$(C_{51}H_{30}N_2O_5)_n$	81.59	80.02	4.03	3.76	3.73	3.35
6d	96	1.15	$(C_{51}H_{30}N_2O_6)_n$	79.88	78.62	3.94	3.48	3.65	3.21
6e	95	1.28	$(C_{52}H_{32}N_2O_5)_n$	81.66	80.48	4.22	3.87	3.66	3.18
6f	96	1.30	$(C_{57}H_{34}N_2O_7)_n$	79.71	78.55	3.99	3.11	3.26	2.95
7a	97	0.92	$(C_{45}H_{30}N_2O_5)_n$	79.63	78.22	4.46	4.12	4.13	3.65
7b	95	0.86	$(C_{45}H_{30}N_2O_5)_n$	79.63	78.96	4.46	4.05	4.13	3.60
7c	97	1.32	$(C_{51}H_{34}N_2O_5)_n$	81.15	80.17	4.54	4.12	3.71	3.08
7d	97	0.82	$(C_{51}H_{34}N_2O_6)_n$	79.47	78.25	4.45	4.02	3.63	3.12

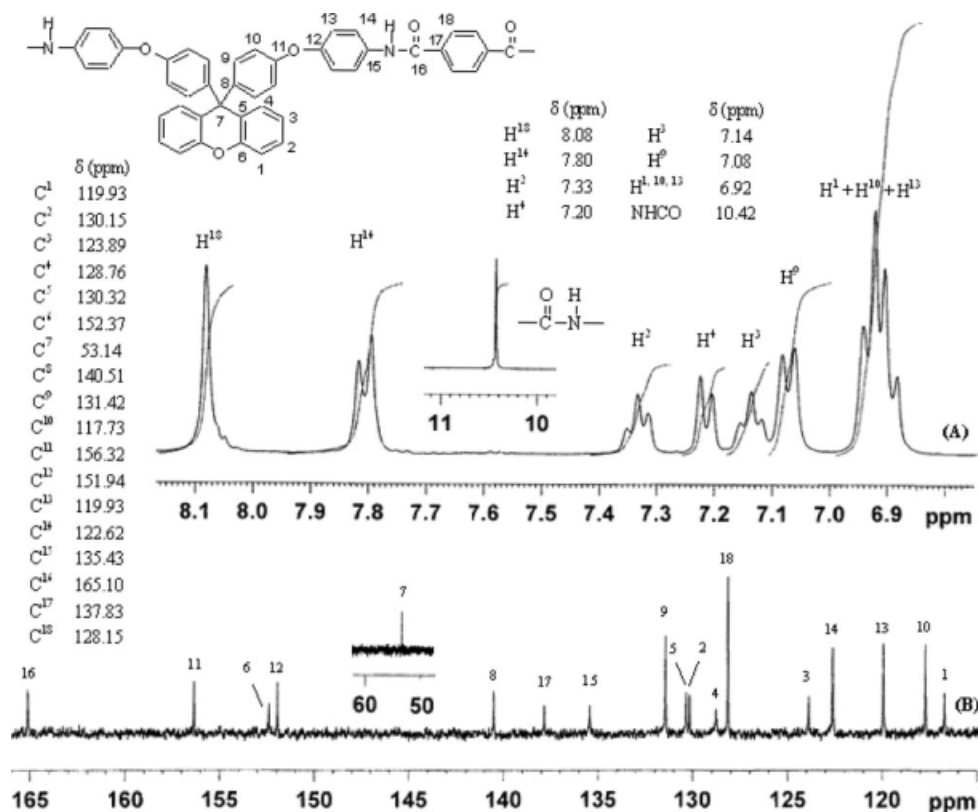[a] Inherent viscosity (η_{inh}) determined at a concentration of 0.5 g/dL in DMAc at 30°C.

Figure 4 ^{1}H-NMR **(A)** and ^{13}C-NMR **(B)** spectra of the polyamide **7a** (DMSO-d_6).

the polyamides did not lose eight below 500°C in nitrogen. The 10% decomposition temperatures both in air and nitrogen atmosphere and the char yield at 800°C in nitrogen are summarized in Table II. The 10% weight loss temperatures is in the range of 502–540°C and 488–515°C in nitrogen and air atmosphere, respectively, and more than 54% weight was retained even at 800°C.

TABLE II
Thermal and Tensile Properties of Polyamides

| Polymer | $T_g{}^a$ (°C) | $T_d{}^b$ (°C) | | Char Yield^c (%) | Tensile Properties^d | | |
		In N$_2$	In air		Tensile strength (MPa)	Elongation to break (%)	Tensile modulus (GPa)
6a	288	525	504	59	95	16	2.48
6b	264	532	510	62	86	13	2.42
6c	302	540	502	67	109	15	2.63
6d	283	535	515	60	100	17	2.40
6e	279	502	488	56	88	14	2.15
6f	272	508	494	57	90	21	2.26
7a	294	520	500	60	98	15	2.38
7b	271	512	498	59	96	18	2.51
7c	308	535	512	64	104	22	2.35
7d	281	521	502	58	102	13	2.30

^{a} The samples were heated to 400°C with a heating rate of 20°C/min and rapidly cooled to 30°C at −100°C/min. The midpoint of baseline shift on the subsequent second DSC heating trace was defined as T_g.
^{b} Decomposition temperatures at which 10% weight loss was recorded by TGA at a heating rate of 20°C/min.
^{c} Residual weight (%) when heated to 800°C at a scan rate of 20°C/min in nitrogen.
^{d} Films were cast from slow evaporation of the polymer solutions in DMAc. The cast films were dried under vacuum at 150°C for 6 h prior to the tensile test.
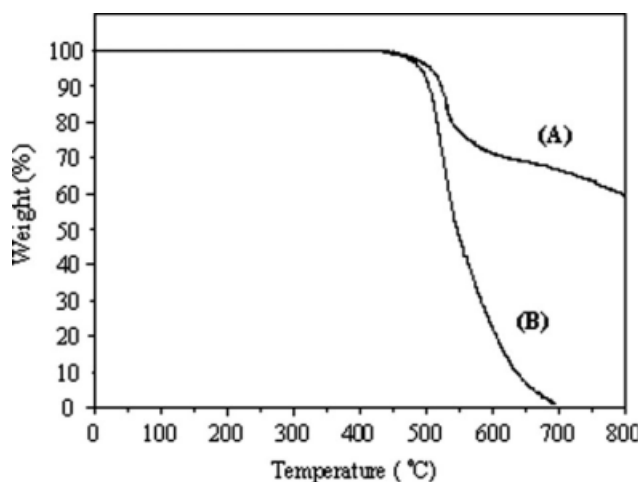
Figure 5 TG curves for aromatic polyamide **6a** in nitrogen **(A)** and air **(B)**.

Mechanical and crystal properties

Strong, transparent and flexible films could be easily obtained from DMAc solutions of these polymers. Their mechanical properties with tensile strengths of 86–109 MPa, elongations at break at 13–22%, and tensile moduli of 2.15–2.63 GPa, shown in Table II, are good and could be used as tough materials. Additionally, as can be seen from Table II, the isomeric polyamides **6a–6d** and **7a–7d** exhibited similar tensile properties.

The wide-angle X-ray diffraction confirmed that all polyamides, even that obtained from *p*-phenylenediamine and benzidine, were completely amorphous. This is reasonable because the presence of bulky pendant structure hindered chain packing and reduced intramolecular interactions. Thus, the amor-

phous nature of these polymers was reflected in their good solubility.

Solubilities of polymers

The solubility of these xanthene-containing polyamides was studied qualitatively, and the results are summarized in the Table III. All polyamides were readily soluble in polar aprotic solvents (such as NMP, DMAc, and DMF), and even in pyridine, and some of them also in DMSO and *m*-cresol. However, almost all of the polymers were insoluble in chloroform, THF, and methanol. These polyamides exhibited higher solubility than the conventional aromatic polyamides, which is attributed to the introduction of bulky xanthene and aryl ether units along the polymer backbone. In addition, in comparison with two sets of analogous polyamides of **6a** and **7a**, which had an isomeric repeat unit, they revealed similar solubility behavior. This indicates that the presence of xanthene in either diamine or dicarboxylic acid moiety did not noticeably affect polymer solubility.

CONCLUSIONS

Two novel monomers of dicarboxylic acid and diamine with xanthene structures were successfully synthesized in high purity and high yields. And the corresponding polyamides with high molecular weight were prepared based on these monomers in good yields. The introduction of the xanthene cardo group and aryl ether groups into aromatic polymer backbones resulted in aromatic polyamides with good thermal stability, as well as excellent solubility in organic solvents. Thus, the present aromatic

TABLE III
Solubility Behavior of Polyamides[a]

Polymer	Solvent[b]								
	NMP	DMAc	DMF	DMSO	*m*-Cresol	THF	MeOH	CHCl₃	Py
6a	++	++	++	+	+	+−	−	−	++
6b	++	++	++	++	++	−	−	−	++
6c	++	++	++	+	+	−	−	−	++
6d	++	++	++	++	++	+−	−	−	++
6e	++	++	++	+	++	−	−	−	++
6f	++	++	++	++	++	−	−	−	++
7a	++	++	++	+	++	+−	−	−	++
7b	++	++	++	++	++	−	−	−	++
7c	++	++	++	+	+	−	−	−	++
7d	++	++	++	++	++	−	−	−	++

[a] Measured at 3.0% (w/v). ++ = soluble at room temperature; + = soluble on heating at 100°C; +− = partially soluble; − = insoluble even on heating.
[b] NMP, *N*-methyl-2-pyrrolidone; DMAc, *N,N*-dimethylacetamide; DMF, *N,N*-dimethylformamide; DMSO, dimethyl sulfoxide; THF, tetrahydrofuran; Py, pyridine.

polymers are considered new candidates for processable high-performance polymeric materials.

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