Polyimides Derived from Mellophanic Dianhydride

Xingzhong Fang, Zhenghua Yang, Suobo Zhang, Lianxun Gao, and Mengxian Ding*

State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences; Polymer Chemistry Laboratory, Chinese Academy of Sciences and China Petro-Chemical Corporation, Changchun, 130022, P. R. of China

Received March 22, 2002; Revised Manuscript Received August 20, 2002

ABSTRACT: The synthesis of mellophanic dianhydride (MPDA), an isomer of pyromellitic dianhydride (PMDA), was studied. A trend of forming cyclic oligomers in the reactions of MPDA with 4,4′-oxydianiline (ODA) or 4,4′-methylenedianiline (MDA) in DMAC was found. The cyclic dimer from MPDA/MDA was isolated and fully characterized, including an X-ray crystallographic analysis. The reactions of MPDA with aromatic diamines were found much more complicated than those of PMDA. A model study was performed to clarify the reactions. Several byproducts were isolated and characterized, so that, in an usual two-step process to prepare polyimides, imide, amide linkage, and carboxylic group may be involved in the polymer structure. The water, either existing in solvent or being generated during the imidization, is the main reason for the side reactions. The properties of some polyimides derived from MPDA and diamines were tested and compared with those of the isomeric polyimides derived from PMDA.

Introduction

Polyimides as a class of thermally stable polymers combined with excellent mechanical properties, dielectric properties, radiation resistance, and processability with various methods have been developed for nearly half a century. Hundreds of polyimides have been synthesized to investigate the relationships between the structure and the properties. Dozens of polyimides possessing different structures have been commercialized to meet various requirements for the applications. Among the structure studies, we are particularly interested in the isomeric effects. As a part of an effort to investigate the isomerism in polymers, polyimides derived from mellophanic dianhydride (MPDA)[1] (Figure 1), as the isomer of commonly known pyromellitic dianhydride (PMDA), were synthesized in our laboratory recently. A great deal of work has been done on the polyimides based on PMDA. The most well-known is that based on PMDA and 4,4′-oxydianiline (ODA), from which, Kapton, a film, and Vespel, a plastic, have been commercialized by Du Pont since the 1960s. However, the polyimides based on mellophanic dianhydride have not attracted much attention, except one patent revealed in the late 1960s by a Japanese group.[2] But in this patent, only copolyimides from PMDA and MPDA with 3,3′-ODA have been reported. The inventors indicated that the copolyimides within the ratio of MPDA to PMDA in 50−85% could dissolve in DMAC, DMF, DMSO, NMP, pyridine, and concentrated sulfuric acid. Another related work was reported by Wang and co-workers;[3] they have synthesized 5,6-diphenyl-1,2,3,4-benzenetetracarboxylic dianhydride and the polyimides therefrom.

In the present article, we will describe the synthetic routes of mellophanic dianhydride, the cyclization, and isomerization found in the reaction of MPDA with diamines. The properties of the polyimides from both mellophanic and pyromellitic dianhydrides will also be revealed for comparison.

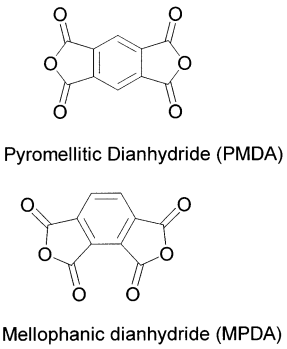


Figure 1. Structures of isomeric dianhydrides.

Experimental Section

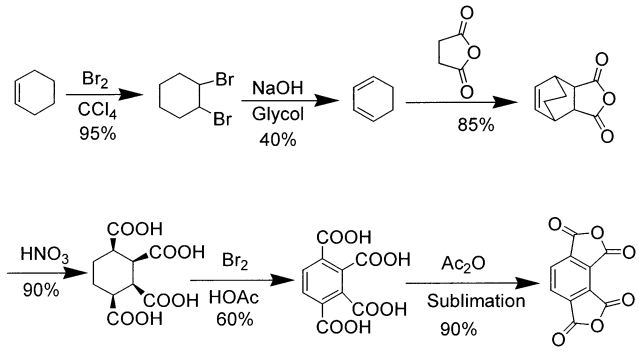
Materials. *p*-Chlorophenol and isoquinoline were purchased from Aldrich Chemical Co. and used as received. 1,8,9-Anthracenetriol (dithranol) was purchased from Linear Scienfific Inc. and used as received. All of the other reagents were from Shanghai Chemical Reagent Plant and were of analytical grade. Tetrahydrofuran (THF) was purified by distillation over sodium chips and benzophenone. *N*,*N*-Dimethylacetamide (DMAc) was purified by distillation over phosphorus pentoxide and stored over 4 Å molecular sieves. Acetic anhydride and triethlylamine (TEA) were used after distillation in the presence of magnesium and calcium hydride, respectively. Aniline was used by distillation under reduced pressure. Pyromellitic dianhydride (PMDA) and 4,4′-oxydianiline (ODA) were purified by sublimation under vacuum. 4,4′-Methylenedianiline (MDA) and 4,4′-diamino-3,3′-dimethyldiphenylmethane (DMMDA) were purified by recrystallization from ethanol prior to use. 4,4′-Bis(4-aminophenoxy)benzene (TPEQ) was prepared from hydroquinone and *p*-chloronitrobenzene in the presence of K_2CO_3 in DMAc, then reduced by Pd/C-H_2, and finally recrystallized from ethanol before use.

Measurements. IR spectra were determined with a Bio-Rad Digilab Division FTS-80 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity spectrometer at 400 and 100 MHz, respectively, with tetramethylsilane (TMS) as

* To whom correspondence should be addressed. E-mail: mxding@ciac.jl.cn.

10.1021/ma0204610 CCC: $22.00
Published on Web 10/10/2002

Scheme 1. Synthesis of Mellophanic Dianhydride (MPDA) from Cyclohexene



an internal standard. Elemental analyses were performed on an Elemental Analyses MOD-1106 (Italyd). Mass spectra were obtained on a Finnigon LCQ mass spectrometer with electrospray voltage at 5.0 kV and capillary temperature at 200 °C. Intrinsic viscosities were determined at 30 °C with an Ostward viscometer, and the concentration were 0.5 g/dL in DMAc or *p*-chlorophenol. UV−vis spectra were recorded on a Cary 1E Varian spectrophotometer. The concentration of samples was 50 μg/mL. Thermogravimetric analyses (TGA) were obtained at a heating rate of 20 °C/min in nitrogen with a Perkin-Elemer TGA-2 thermogravimetric analyzer. The differential scanning calorimetry (DSC) experiments were carried out on a Perkin-Elmer DSC-7 system at a heating rate of 10 °C/min under a nitrogen atmosphere. The wide-angle X-ray diffraction (WAXD) measurements were undertaken on a Philos X-ray diffractometer with Cu−K radiation (40 kV, 30 mA) with a scanning rate of 2°/min. The tensile measurements were carried out on an Instron model 1122 at room temperature. MALDI−TOF mass spectra were recorded on a LDI-1700 mass spectrometer (Linear Scienfific Inc.) equipped with delayed extraction. A 337 nm nitrogen laser producing 3 ns pulses was used, and the instrument was operated in the positive reflection mode with an accelerating potential of 20 kV and an extraction delay of 50 ns. Samples were prepared by mixing 10 μL of dimethyl sulfoxide (DMSO) of the oligomer sample (2 g L^{-1}) with 50 μL of a solution of 15 g L^{-1} 1,8,9-anthracenetriol (dithranol) in DMSO.

Single-crystal X-ray diffraction data were collected at 293(2) K on a Rigaku R-AXIS RAPID diffractometer (λ = 0.710 73 Å). The structure was solved by the direct method using the SHELXTL system[4] and refined by a full matrix least squares on F^2 using all reflections.

Synthesis of Mellophanic Dianhydride. The synthesis of 1,2,3,4-benzenetetracarboxylic acids was reported in the literature.[5−7] Mellophanic dianhydride (MPDA) was synthesized by following a method described in the literature[8] (Scheme 1).

1,2,3,4-Benzenetetracarboxylic acids: mp 224−226 °C (lit.[7] 241−244 °C). IR (KBr): 1698 cm^{-1} (carboxylic acids). ^{1}H NMR (400 MHz, D_2O): δ (ppm) 7.980 (s, ArH). ^{13}C NMR (100 MHz, D_2O): δ 170.04, 167.08, 132.17, 131.36, 130.69. MS: Calcd for $C_{10}H_6O_8$ 254.15. Found $[M + H]^+$ = 255.41, Elemental analysis: Calcd for $C_{10}H_6O_8$: C, 47.26; H, 2.38%. Found: C, 46.54; H, 2.15%.

MPDA: mp 198−200 °C (lit.[8] 196−197 °C). IR (KBr): 1857, 1816, 1795, 1780 cm^{-1} (aromatic dianhydride). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 8.673 (s, ArH). ^{13}C NMR (100 MHz, DMSO-d_6): 161.17, 157.98, 138.06, 132.22, 128.05. MS Calcd for $C_{10}H_2O_6$ 218.12. Found: $[M + H]^+$ = 219.03. Elemental analysis: Calcd for $C_{10}H_6O_8$: C, 55.07; H, 0.92%. Found: C, 55.22; H, 0.86%.

Reaction of Model Compounds. Method A (Scheme 8): A mixture of aniline (0.5310 g, 2.85 mmol) and MPDA (0.6218 g, 2.85 mmol) was reacted in DMAc (15 mL) with stirring under a nitrogen atmosphere at room temperature for 6 h. Toluene (5 mL) was added, the mixture was heated and refluxed for 4 h, and water was removed as the toluene/water azeotrope via a Dean−Stark trap. After an additional refluxing for 12 h, the resulting solution was poured into 200 mL of distilled water; the precipitate was filtered off, washed thoroughly with water, and dried at 120 °C for 24 h under vacuum. The solid was chromatographed through a silica gel column eluting with acetonitrile−CH_2Cl_2 (gradient elution, 20−50% acetonitrile). The product diimide **1** and monoimide **2** (Scheme 8) were obtained as yellow crystals. **1** (0.64 g, 63% yield): mp 283−284 °C. IR (KBr): 1776, 1734, 1369, 728 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 8.40 (s, 2H), 7.59−7.47 (m, 10H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 165.73, 163.24, 137.28, 131.60, 128.99, 128.70, 128.49, 128.10, 127.46. MS: Calcd for $C_{22}H_{12}O_4N_2$ 368.35. Found $[M + H]^+$ 369.32. UV−vis (acetone, λ_{max}): 337 nm. Elemental analysis: Calcd for $C_{22}H_{12}O_4N_2$: C, 71.72; H, 3.29; N, 7.61%. Found: C, 71.72; H, 3.24; N, 7.74%.

2 (0.20 g, 20% yield): mp 253−254 °C. IR (KBr): 1754, 1739, 1688, 1660, 1399, 724 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 10.68 (s, 1H), 8.13−8.11 (d, 1H), 8.07−8.05 (d, 1H) 7.69−7.11 (m, 10H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 166.75, 165.40, 164.54, 162.78, 138.66, 135.03, 134.23, 132.89, 132.70, 131.49, 128.99, 128.89, 128.69, 128.43, 127.69, 127.49, 124.06, 119.65. MS: Calcd for $C_{22}H_{14}O_5N_2$ 386.36. Found $[M + H]^+$ 387.43. UV−vis (acetone, λ_{max}): 331 nm. Elemental analysis: Calcd for $C_{22}H_{14}O_5N_2$: C, 68.39; H, 3.65; N, 7.25%. Found: C, 68.34; H, 3.64; N, 7.39%. A suitable single crystal for monoimide **2** was obtained from CH_2Cl_2/*n*-hexane solution. Crystal data for monoimide **2**: $C_{22}H_{14}O_5N_2$, fw = 386.35, monoclinic, *P*-1, a = 6.898(2) Å, b = 11.583(0) Å, c = 12.194(2) Å, α = 66.824(9)°, β = 88.561(1)°, γ = 88.097(6)°, V = 895.1(2) Å^3, Z = 2, T = 293(2) K, $R_1(I>2\sigma(I))$ = 0.0632, ωR_2 (all data) = 0.1298, GOF = 0.861.

Method B (Scheme 8): A typical procedure is as follows: The amic acid was prepared as mentioned above. Acetic anhydride (4 mL) and triethylamine (2 mL) were added to the amic acid solution. The reaction mixture was stirred for 24 h at room temperature. The resulting solution was poured into 200 mL of distilled water; the precipitate was filtered off, washed thoroughly with water, and dried at 140 °C for 12 h under vacuum. The diimide **1** was obtained in almost quantitative yield.

Method C (Scheme 8): A mixture of the MPDA (1.3116 g, 6.01 mmol), aniline (1.1200 g, 6.01 mmol), and a few drops of isoquinoline in *p*-chlorophenol (40 mL) was stirred at 200 °C under nitrogen for 18 h. The resulted solution was poured slowly into methanol (300 mL) with stirring. The precipitate was collected by filtration and extracted with methanol in a Soxhlet extractor for 6 h and dried at 140 °C for 12 h under vacuum to afford diimide **1** (2.16 g, 98% yield).

Synthesis of Cyclic Oligomers. Cyclic Oligomers and Cyclic Dimer from 4,4′-Methylenedianiline (MDA). A solution of MPDA (0.8581 g, 3.93 mmol) in DMAc (40 mL) and a solution of MDA (0.7800 g, 3.93 mmol) in DMAc (40 mL) were delivered into a mechanically stirred flask containing 120 mL of DMAc over a 2 h period. After the addition, the mixture was stirred for another 2 h to ensure complete reaction. Then acetic anhydride (5 mL) and triethylamine (3 mL) were added. The temperature was gradually elevated to 50 °C. After 24 h reaction, the solution was concentrated to about 20 mL under reduced pressure and poured into distilled water. The precipitate was filtered off, washed thoroughly with water, and dried at 120 °C for 12 h under vacuum. After extraction in a Soxhlet extractor with 250 mL of chloroform for 12 h, the solution was concentrated to 10 mL and added to a vigorously stirred methanol (100 mL). The product as a yellow solid was filtered and dried in a vacuum oven at 120 °C for 12 h with a yield of 0.40 g (27% yield). The MALDI−TOF mass spectrum is shown in Figure 2. The cyclic dimer of **3a** was obtained by recrystallization from chloroform (0.08 g, 4% of total yield). IR (KBr): 1776, 1724, 1364, 724 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 8.33 (s, 2H), 7.48−7.16 (m, 8H), 4.02 (s, 2H). MALDI−TOF-MS: Calcd for $C_{46}H_{24}O_8N_4$ 760. Found $[M + H]^+$ 761. A single crystal of cyclic dimer **3a** was obtained from chloroform/*n*-hexane solution. Crystal data for cyclic dimer **3a**: $C_{46}H_{24}O_8N_4 \cdot 2CHCl_3 \cdot 6H_2O$, fw = 1107.52, orthorhombic, *Pccn* (No. 56), a

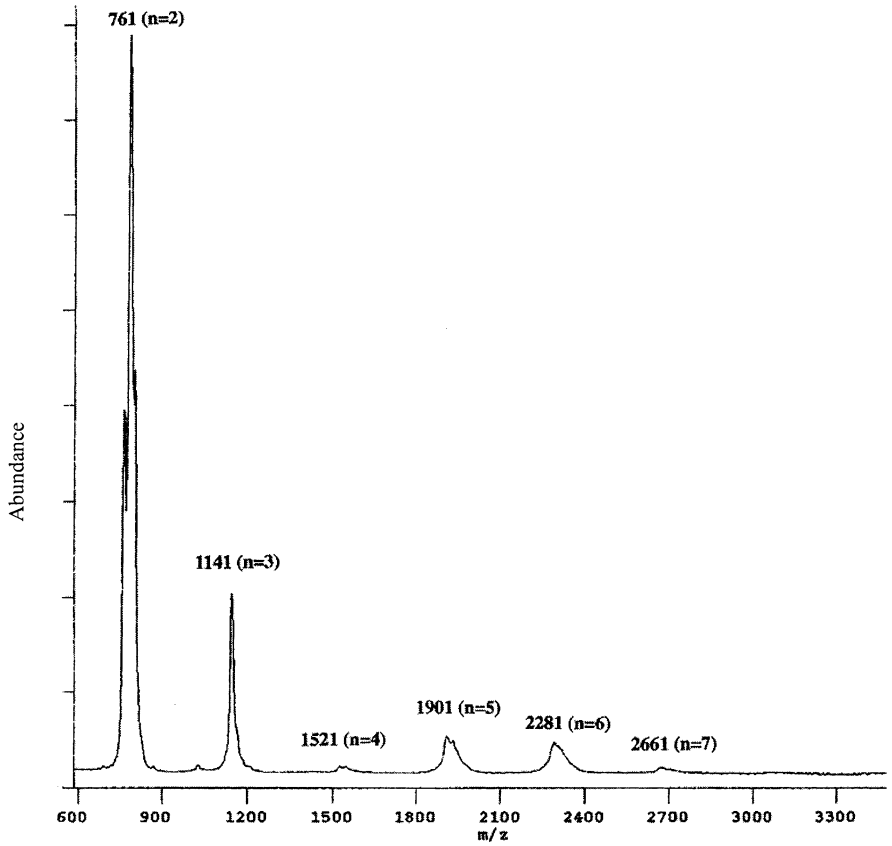


Figure 2. MALDI−TOF-MS spectrum of cyclic oligomers derived from MPDA/MDA using 1,8,9-anthracenetriol as matrix.

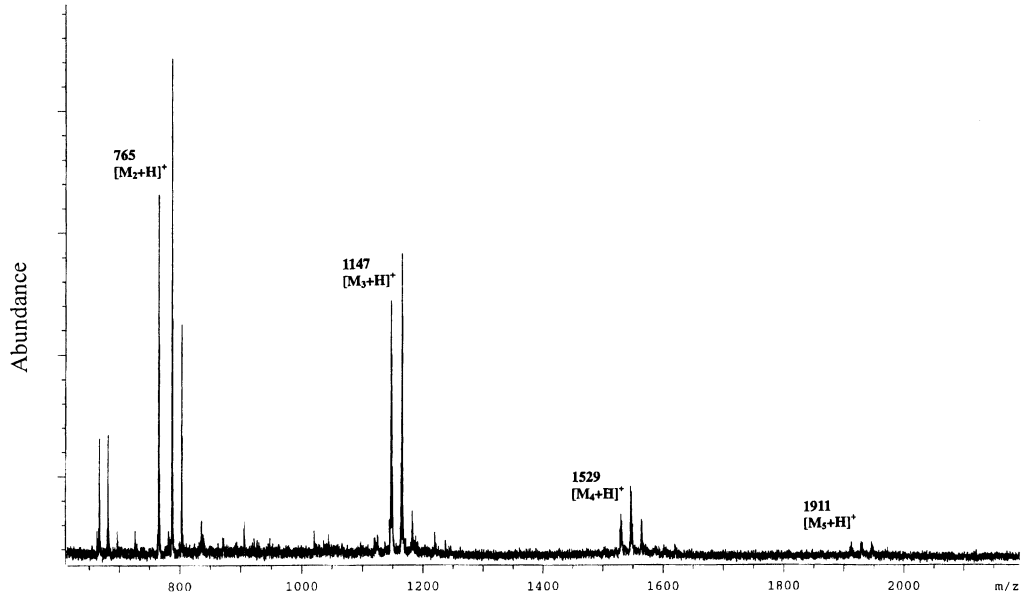


Figure 3. MALDI−TOF-MS spectrum of cyclic oligomers derived from MPDA/ODA using 1,8,9-anthracenetriol as matrix.

= 16.901(3) Å, b = 27.376(6) Å, c = 11.605(2) Å, $\alpha = \beta = \gamma$ = 90°, V = 5369.2(19) Å^3, Z = 4, T = 293(2) K, $R_1(I>2\sigma(I))$ = 0.0653, ωR_2 (all data) = 0.1519, GOF = 0.934.

Cyclic Oligomers from 4,4′-Oxydianiline (ODA). The same procedure was used as for **3a**, but using MPDA (0.9388 g, 4.31 mmol) and ODA (0.8618 g, 4.31 mmol) as starting materials. The yield of cyclic oligomers of **3b** was 0.30 g (18% yield). IR (KBr): 1775, 1726, 1369, 724 cm^{-1}. The MALDI−TOF-MS spectrum is shown in Figure 3.

Polymers. Polymer 4a. 4,4′-Diamino-3,3′-dimethyldiphenylmethane (DMMDA) (1.0000 g, 4.42 mmol) and DMAc (15 mL) were charged in a 50 mL three-necked, round-bottomed flask equipped with a mechanical stirrer and dry nitrogen gas inlet. After the dissolving of DMMDA, MPDA (0.9638 g, 4.42 mmol) was delivered as a solid into the flask over 0.5 h. After stirring at room temperature for 12 h, the white precipitate was formed in the viscous solution. Then acetic anhydride (4 mL) and triethylamine (2 mL) were added, as the reaction progressed for 24 h, a brown viscous solution resulted. An aliquot of the polymer solution was taken out and purified by precipitated in ethanol and redissolved in DMAC for three times and then cast on a glass plate and dried at 80 °C for 18 h, followed by heating at 150 °C (1 h), 200 °C (1 h), 250 °C (1 h), and 300 °C (1 h) to afford polyimide film. The

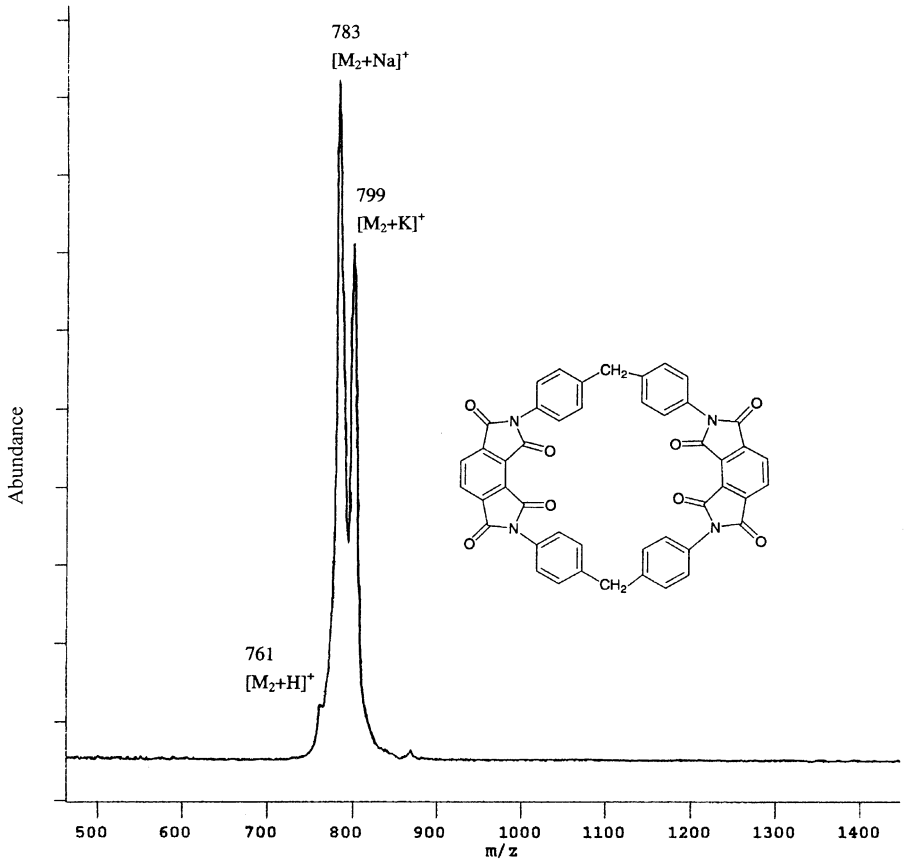


Figure 4. MALDI−TOF-MS spectrum of cyclic dimer of **3a** using 1,8,9-anthracenetriol as matrix.

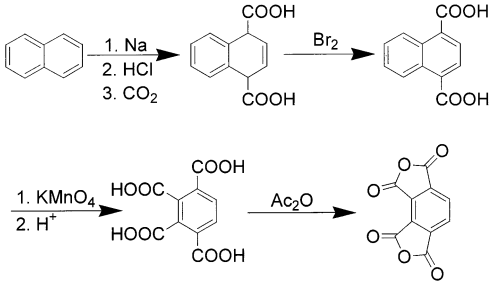
remaining polymer solution was poured slowly into 200 mL of methanol with stirring. The precipitate was collected by filtration and extracted with methanol in a Soxhlet extractor for 6 h and dried under vacuum to afford soluble polyimide of **4a** (0.85 g, 95%). IR (KBr): 1776, 1728, 1365, 727 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ (ppm) 8.40 (s, 2H), 7.35−7.27 (m, 8H), 4.04 (s, 2H), 2.13 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6): 165.63, 163.15, 142.13, 137.21, 136.25, 131.02, 129.07, 128.63, 128.33, 127.03, 39.92, 17.39. UV−vis (DMAc, λ_{max}): 275 nm. Elemental analysis: Calcd for $(C_{25}H_{16}O_4N_2)_n$: C, 71.72; H, 3.29; N, 7.61%. Found: C, 70.95; H, 4.10; N, 7.08%.

Polymer 4b. A mixture of MPDA (0.7461 g, 3.42 mmol), the 1,4-bis(4-aminophenoxy)benzene (TPEQ) (1.0000 g, 3.42 mmol), and a few drops of isoquinoline in *p*-chlorophenol (40 mL) was stirred at 200 °C under nitrogen for 18 h. The viscous solution was poured slowly into methanol (400 mL) with stirring. The fibrous polymer was collected by filtration and extracted with methanol in a Soxhlet extractor for 6 h and dried under vacuum. The yellowish insoluble polyimide of **4b** (1.58 g, 98%) was obtained. IR (KBr): 1775, 1732, 1367, 723 cm^{-1}. Elemental analysis: Calcd for $(C_{28}H_{14}O_4N_2)_n$: C, 76.01; H, 3.19; N, 6.33%. Found: C, 75.88; H, 3.49; N, 5.75%.

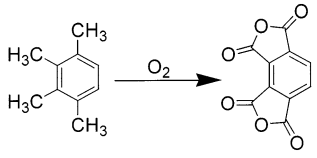
Polymer 5a. Polymerization of PMDA with DMMDA was performed similarly to the case of **4a** to give soluble polyimide of **5a** as a yellow powder in 95% yield: IR (KBr): 1779, 1726, 1373, 728 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ (ppm) 8.40 (s, 2H), 7.35−7.27 (m, 8H), 4.04 (s, 2H), 2.13 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6): 165.43, 142.24, 137.13, 136.28, 131.12, 129.11, 128.57, 127.11, 118.24, 40.12, 17.44. UV−vis (DMAc, λ_{max}): 275 nm. Elemental analysis: Calcd for $(C_{25}H_{16}O_4N_2)_n$: C, 71.72; H, 3.29; N, 7.61%. Found: C, 70.92; H, 3.49; N, 6.73%.

Polymer 5b. Polymerization of PMDA with TPEQ was performed similarly to the case of **4b** to give **5b** as a yellow powder in 98% yield. IR (KBr): 1779, 1726, 1373, 728 cm^{-1}. Elemental analysis: Calcd for $(C_{28}H_{14}O_4N_2)_n$: C, 76.01; H, 3.19; N, 6.33%. Found: C, 75.33; H, 3.58; N, 6.29%.

Scheme 2. Synthesis of MPDA from Naphthalene



Scheme 3. Synthesis of MPDA from Prehnitene



Results and Discussion

Synthesis of Mellophanic Dianhydride. There are three approaches for the synthesis of mellophanic dianhydride as is shown in Schemes 1−3: from cyclohexadiene[8] or cyclohexene (Scheme 1), from naphthalene[6,7] (Scheme 2), and from prehnitene[5] (Scheme 3).

We synthesized mellophanic dianhydride (MPDA) in a total of six steps from cyclohexene as a starting material in modest yield (Scheme 1). The 1,3-cyclohexadiene was easily prepared with an excess of sodium hydroxide in boiling ethylene glycol.[9] The subsequent steps involved the Diels−Alder reaction with maleic anhydride, followed by oxidation with nitric acid, aro-

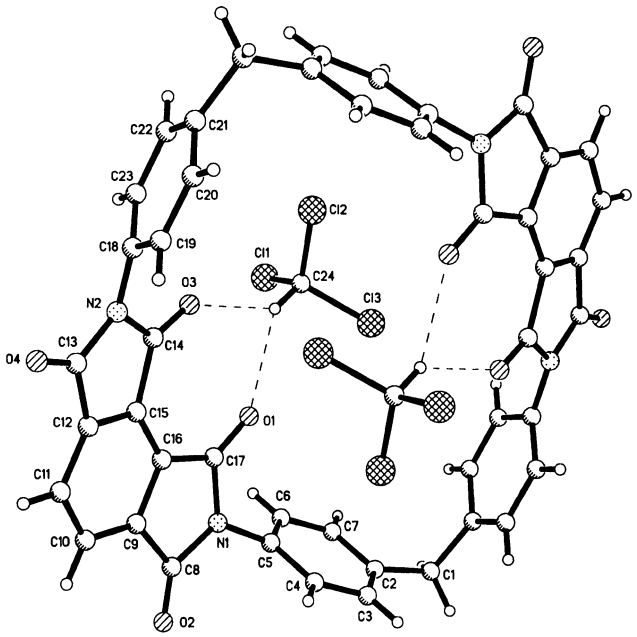


Figure 5. Crystal structure of cyclic dimer of **3a** for $C_{46}H_{24}O_8N_4 \cdot 2CHCl_3 \cdot 6H_2O$, showing the intramolecular hydrogen bonds in one dimer (H_2O molecules are omitted for clarity).

matization with bromine, and dehydration.[8] The second route in Scheme 2 suffers from tedious workup and poor yield. The third route is most promising, because prehnitene can be separated from heavy gasoline fraction.[10]

Cyclic Oligomers. When MPDA reacted with ODA or MDA in DMAC at room temperature, precipitates of cyclic oligomers were formed (Scheme 4). Cyclic oligomers of **3a** and **3b** were then obtained by solvent extraction with chloroform in the yields of 27% and 18%, respectively. MALDI−TOF-MS spectra (Figures 2 and 3) indicated that cyclic oligomers of **3a** and **3b** consist principally of macrocycles with repeating units of 2−7 and 2−5, respectively. A typical spectrum of MALDI of **3b** is shown in Figure 3; by using 1,8,9-dithranol as matrix, a relatively clean positive spectrum with excellent signal-to-noise ratio was obtained for the reaction product without addition of any cationization agents. The MALDI−TOF-MS spectrum gives the correct protonated molecular ion peaks for the cyclic oligomers from dimer ($n = 2$) to pentamer ($n = 5$). The expanded scale of the MS spectrum of **3b** shows three signals for each oligomer. For example, signals for the cyclic trimer are located at 1147, 1169, and 1185 Da. The signal at 1147 Da corresponds to the protonated molecular ion peak and that at 1169 Da is due to the adduct of the cyclic trimer with a sodium cation, while that at 1185 Da is due to the adduct with a potassium cation.

The structure of cyclic dimer based on MPDA/MDA was unambiguously confirmed by MALDI−TOF-MS, NMR, FT-IR, and single-crystal X-ray analysis. The MALDI−TOF-MS spectrum of cyclic dimer of **3a** is illustrated in Figure 4. The single-crystal X-ray analysis demonstrated that cyclic dimer is complexed with 2 mol of chloroform, and six H_2O molecules are found in the circumferences of **3a** (omitted in the structure), as is shown in Figure 5. The correct elemental analysis was not easily obtained because of the easy eliminating of the $CHCl_3$ and H_2O molecules in the crystal**.** No melting point could be found up to 400 °C. A detailed description of the structure will be published elsewhere.

Reaction of MPDA with Diamines. As mentioned above, the reactions of MPDA with MDA and ODA generated cyclic oligomers with the member of 2−7 and 2−5, respectively, and the conventional high molecular weight polyamic acids could not be obtained. Principally, three isomers can be generated during polyamic acids stage, two are called as symmetric moieties, and the other asymmetric one (Scheme 5). The symmetric amic acids may be imidized to diimide; however, except diimide, amide−imide can also be obtained from asymmetric amic acid (Scheme 5). This consideration was confirmed by the IR spectra of polymers from MPDA/ODA (Figure 6); spectra a and c are the cyclic oligomers and polyimides prepared by chemical imidization in DMAc at room temperature and thermal imidization in

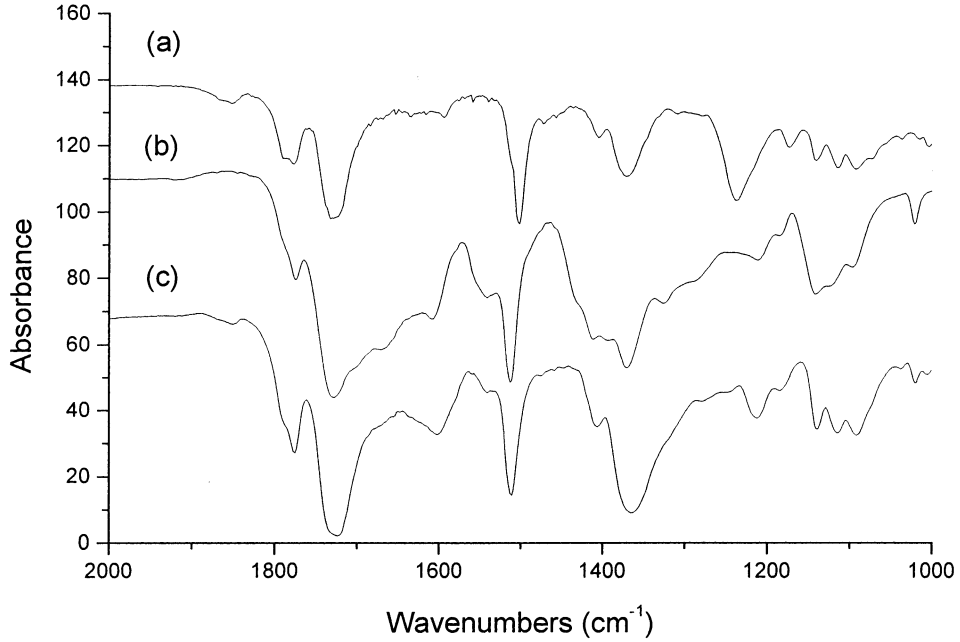
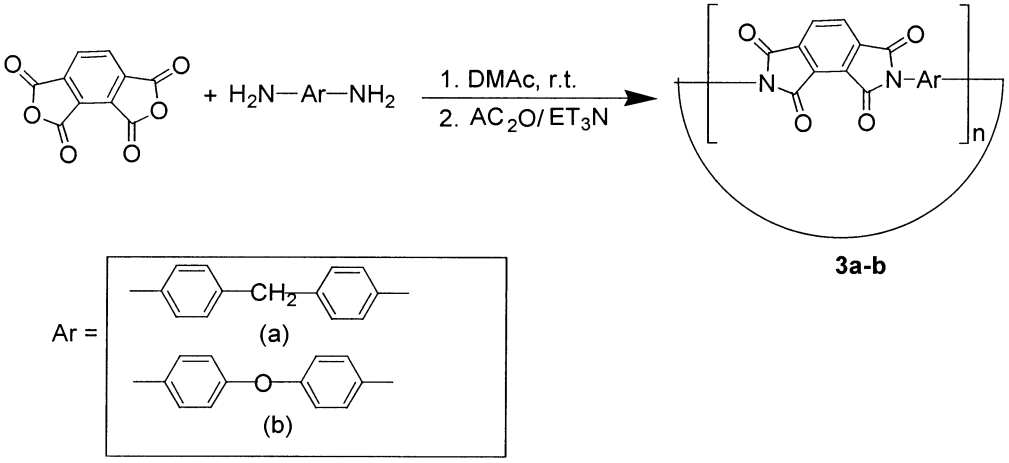
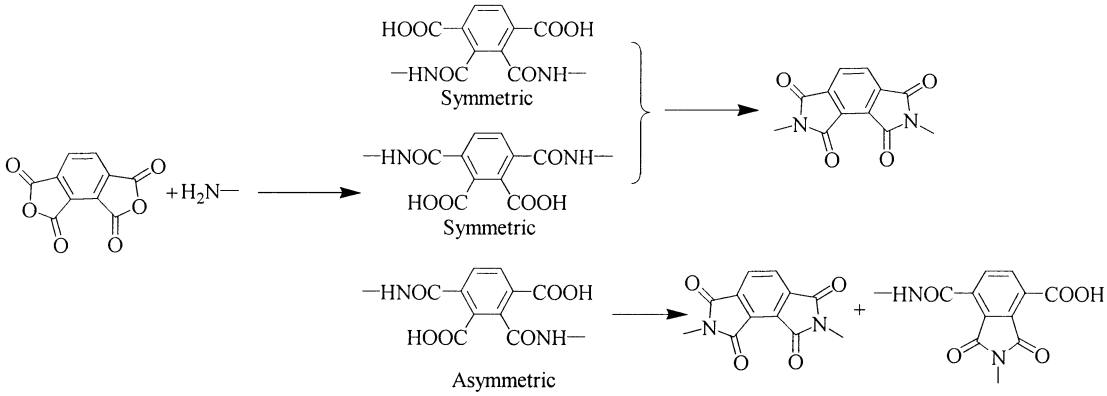


Figure 6. IR of polyimides based on MPDA/ODA: (a) cyclic oligoimides chemically imidized in DMAc, (b) polyimides thermally imidized in DMAc, (c) polyimides thermally imidized in *p*-chlorophenol.

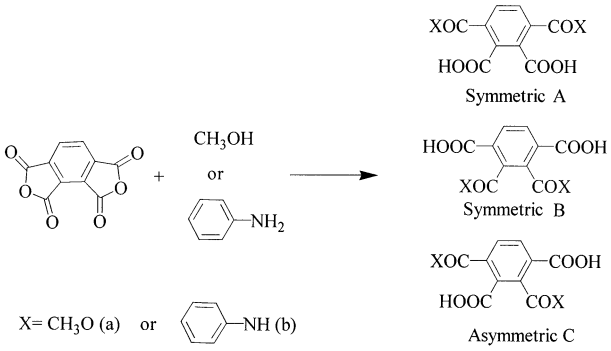
Scheme 4. Synthesis of Cyclic Oligomers



Scheme 5. Imidization of the Isomeric Amic Acids from MPDA



Scheme 6. Esterification and Amidization of MPDA with Methanol or Aniline



p-chlorophenol at 200 °C, respectively. They have normal characteristics of the imide rings. However, in spectrum b, the polymers were obtained by thermal imidization in DMAc; we found complicated features in the 1660−1770 cm^{-1} region. This implied that amide structures existed in the polymers.

Model Reaction of MPDA with Aniline. A further study was carried out by model reaction. The esterification for MPDA in methanol was completed by refluxing for 2 h; nearly quantitative asymmetric dimethyl ester C(a) was obtained (Scheme 6). The structure of C(a) was confirmed by NMR, IR, MS, and elemental analyses.[11]

However, when treatment of MPDA with aniline in DMAC at room temperature, almost quantitative symmetric amic acid B(b) was formed (Scheme 6). The structure of symmetric B(b) was confirmed by NMR, IR, MS, and elemental analyses.[12] The different selectivity between esterification and amidation can be attributed to the formation of cyclic hydrogen bond intermediate in the amidation reaction, in which the nucleophilic amine preferably attack the carbonyl group at C-3 rather than at C-4 (Scheme 7).

Table 1. Model Compounds Reaction of MPDA and Aniline in DMAc at Different Temperatures

entry	temp (°C)	time (h)	product	yield[a] (%)	product	yield[a] (%)
1	80	12	2	70	1	5
2	130	12	2	63	1	12
3	180	18	2	20	1	63

[a] Isolated yield, separated by silica gel column chromatography eluting with acetonitrile−CH_2Cl_2 (gradient elution, 20−50% acetonitrile).

Furthermore, during the thermal imidization of symmetric amic acid B(b) in DMAc by heating, two compounds can be separated by a silica gel column from the product: one was the desired diimide **1**, and the other was the amide−imide **2** (see Scheme 8). As is shown in Table 1, thermal imidization of symmetric B(b) in DMAc at 80 °C gave the major product of monoimide **2**; however, at temperatures of 180 °C or above, the major product was diimide **1**. It is believed that **2** is the product of kinetic controlled, whereas **1** is of thermodynamic controlled. The structures of these model compounds were confirmed by IR, NMR, MS, UV−vis, single-crystal X-ray diffraction, and elemental analyses. Comparing the IR spectra of model compounds, monoimide **2** concurrently showed the characteristic absorption bands of imide ring and amide acid at 1754 (asym C═

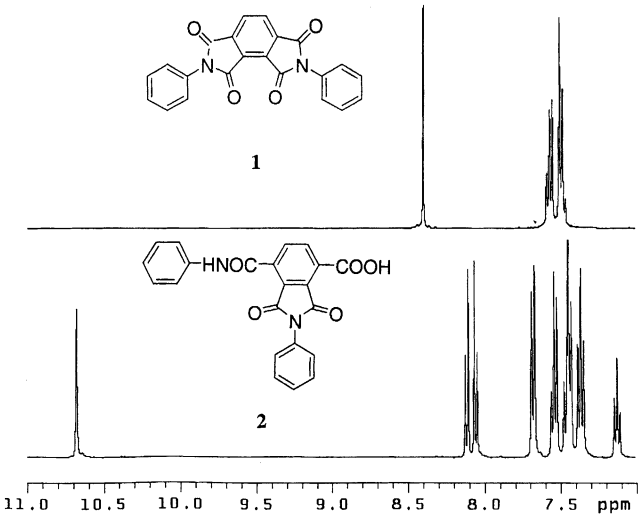


Figure 7. ^{1}H NMR spectra (in DMSO-d_6 with TMS) of diimide **1** and monoimide **2**.

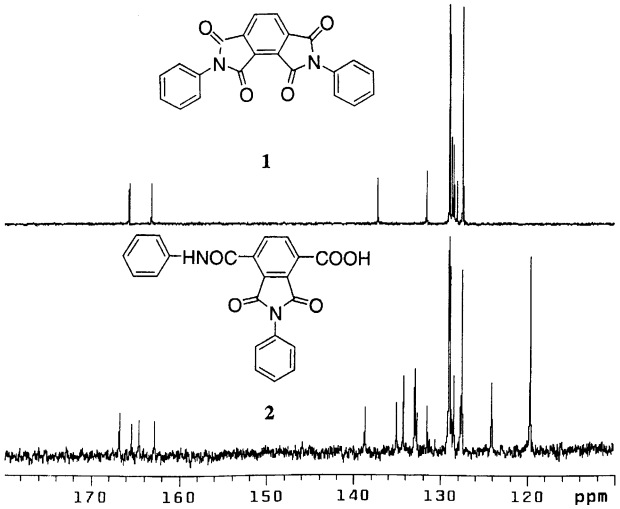


Figure 8. ^{13}C NMR spectra (in DMSO-d_6 with TMS) of diimide **1** and monoimide **2**.

O stretching), 1739 (sym C═O stretching), 1688 (C═O carboxylic acid), 1660 (C═O amide), 1399 (C−N stretching), and 724 cm^{-1} (imide ring deformation); diimide **1** showed only the characteristic absorption bands of imide ring at 1776 (asym C═O stretching), 1734 (sym C═O stretching), 1369 (C−N stretching), and 728 cm^{-1} (imide ring deformation). The ^{1}H NMR spectra of **1** and **2** are shown in Figure 7; a single proton resonance for the amide **2** appears at 10.68 ppm, while the amide proton resonance is no longer observed in the NMR spectrum of **1**. The ^{13}C NMR spectra (Figure 8) are also consistent with the structures of compounds **1** and **2**. The spectrum of **2** shows four carbon resonances at 166.75, 165.40, 164.54, and 162.78 ppm typical of different carbonyl carbons, while **1** shows only two different carbon

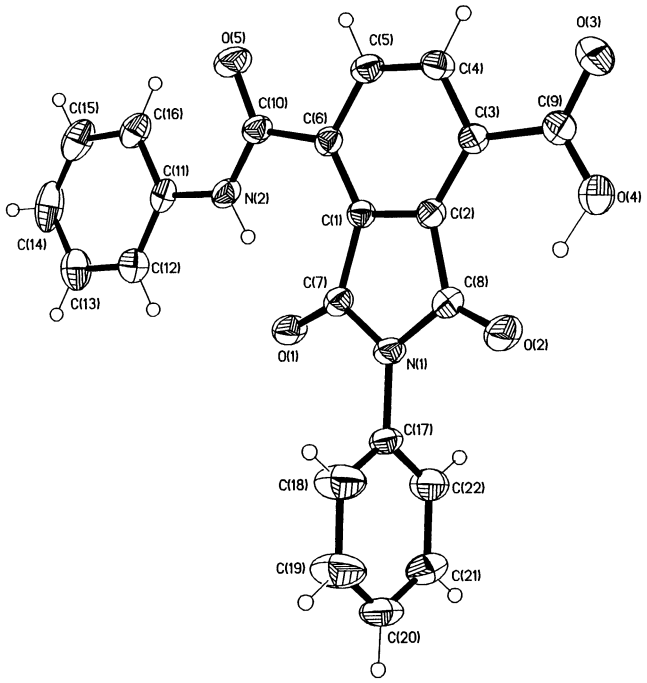


Figure 9. Molecular structure of monoimide **2**.

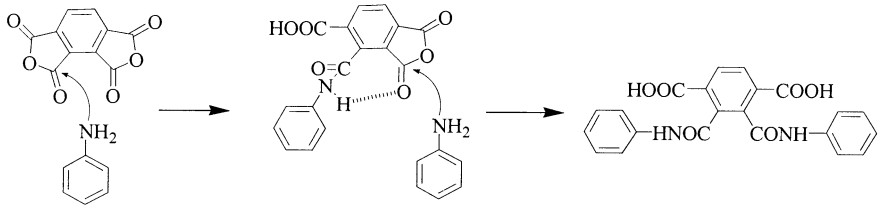
resonances for the imide at 165.73 and 163.24 ppm. UV spectra indicated that monoimide **2** (acetone, $\lambda_{max} = 331$ nm) has a lower degree of conjugation than diimide **1**(acetone, $\lambda_{max} = 337$ nm). The molecular structure of monoimide **2** is shown in Figure 9. MS and elemental analyses further confirmed the structures of model compounds **1** and **2**.

When the amic acid was imidized by chemical imidization using excess acetic anhydride and triethylamine as the dehydrate, only the pure diimide **1** was obtained (Scheme 8). Also, when the polymerization was carried out in *p*-chlorophenol in the presence of a catalyst of isoquinoline at 200 °C, the diimide **1** was obtained in almost quantitative yield (Scheme 8).

This solvent effect can be attributed to the fact that water is miscible with DMAc but not with *p*-chlorophenol and can also not exist in a medium in which acetic anhydride is presented, and the water, either existing in the solvent or being generated during the imidization, can hydrolyze the formed monoimide or diimide to generate the symmetric and asymmetric amic acid; the latter would imidize partly to monoimide (see Scheme 9). Then the symmetric B(b) type of amic acid can also form dicarboxylic monoimide by eliminating the amine during the thermal imidization.[3]

The thermal conversion of **2** to **1** was also conducted at 320 °C under vacuum or in nitrogen atmosphere. In fact, **2** could not convert to **1** under these conditions. This result further proved that water in DMAc played an important role in the thermal conversion of **2** to **1**.

Scheme 7. Proposed Mechanism for Amidization of MPDA and Aniline in DMAc



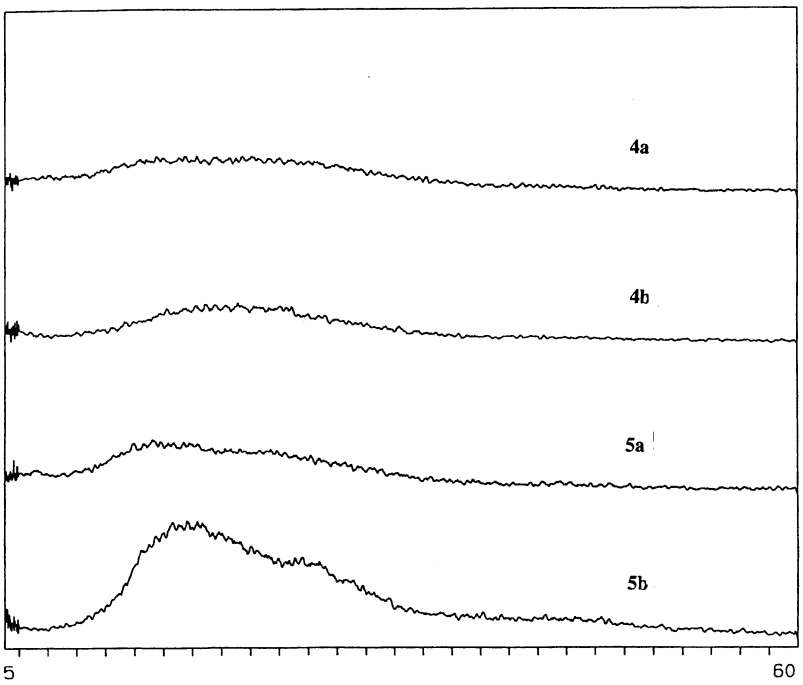


Figure 10. WAXD curves for isomeric polyimides **4a**, **4b**, **5a**, and **5b**.

Scheme 8. Model Reactions of MPDA and Aniline

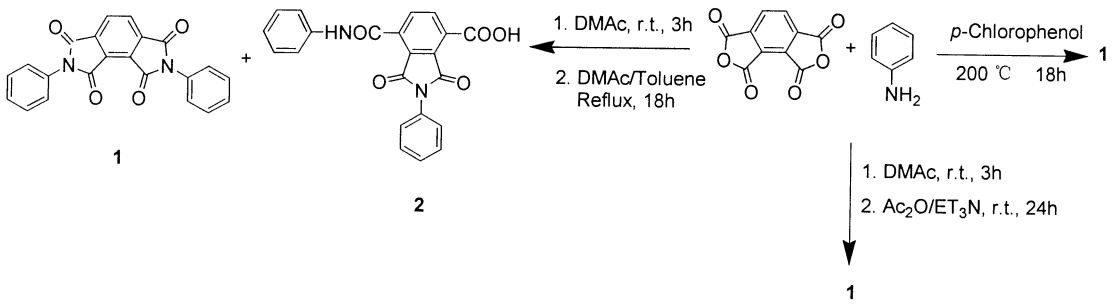


Table 2. Properties of Isomeric Polyimides

polymer	η_{inh} (dL/g)	T_g[c] (°C)	$T_{5\%}$[d] (°C)	modulus (MPa)	tensile strength (MPa)	elongation (%)
4a	0.78[a]	354	482	1682	58	2.8
4b	1.87[b]	292	492			
5a	1.20[a]	274	495	1320	40	3.0
5b	1.38[b]	272	527			

[a] Intrinsic viscosity measured with 0.5 g/dL in DMAc at 30 °C. [b] Intrinsic viscosity measured with 0.5 g/dL in *p*-chlorophenol at 30 °C. [c] Obtained from DSC at a heating rate of 10 °C/min in N_2. [d] 5% weight loss in N_2 at a heating rate of 20 °C/min.

Table 3. Solubilities of Isomeric Polyimides[a]

polymer	$CHCl_3$	TCE[b]	DMAc	DMSO	NMP	*m*-cresol	*p*-chlorophenol	H_2SO_4
4a	+	+	+	+	+	+	+	+
4b	−	−	−	−	−	±	+	+
5a	+	+	+	+	+	+	+	+
5b	−	−	−	−	−	±	+	+

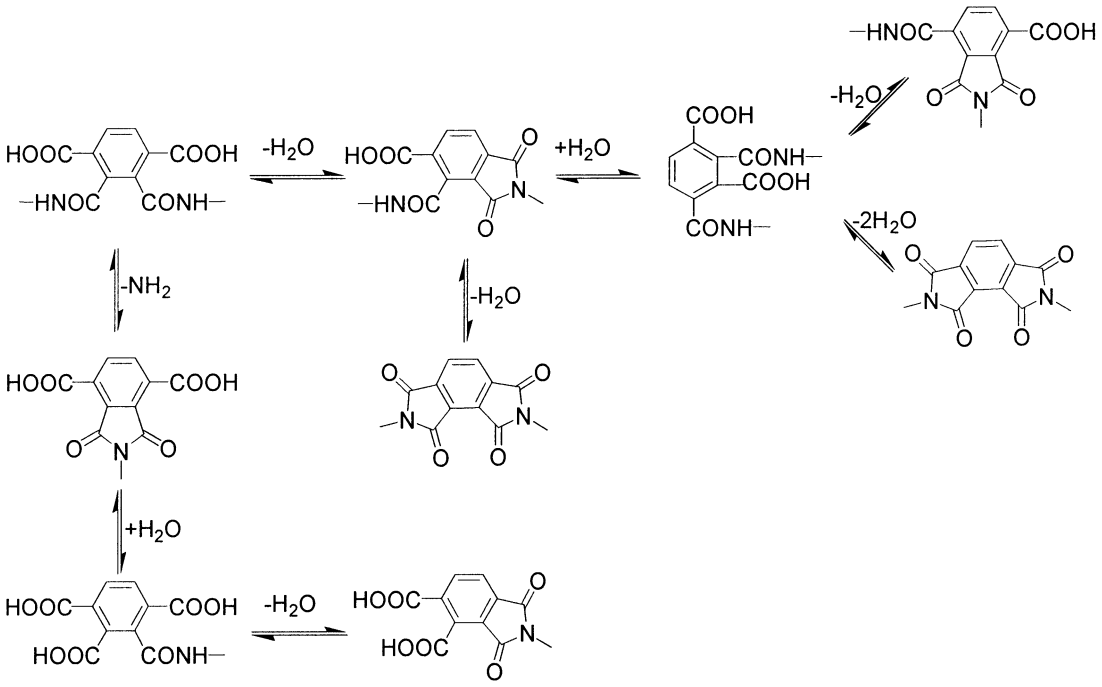
[a] Key: +, fully soluble; ±, partially soluble; −, insoluble on heating. [b] TCE = 1,1,2,2-tetrachloroethane.

Polymers. Based on model reactions, one-step solution polymerization of the MPDA with the diamine (TPEQ) was carried out in *p*-chlorophenol in the presence of a catalytic amount of isoquinoline at 200 °C (Scheme 10). Water formed during the imidization was continuously removed with a stream of nitrogen. A soluble polyimide based on MPDA/DMMDA **4a** was obtained by chemical imidization, although precipitations occurred during the amide acid stage. The corresponding polyimides of **5a** and **5b** were obtained following the same method for **4a** and **4b**, respectively. The properties of isomeric polyimides based on MPDA and PMDA were illustrated in Table 2.

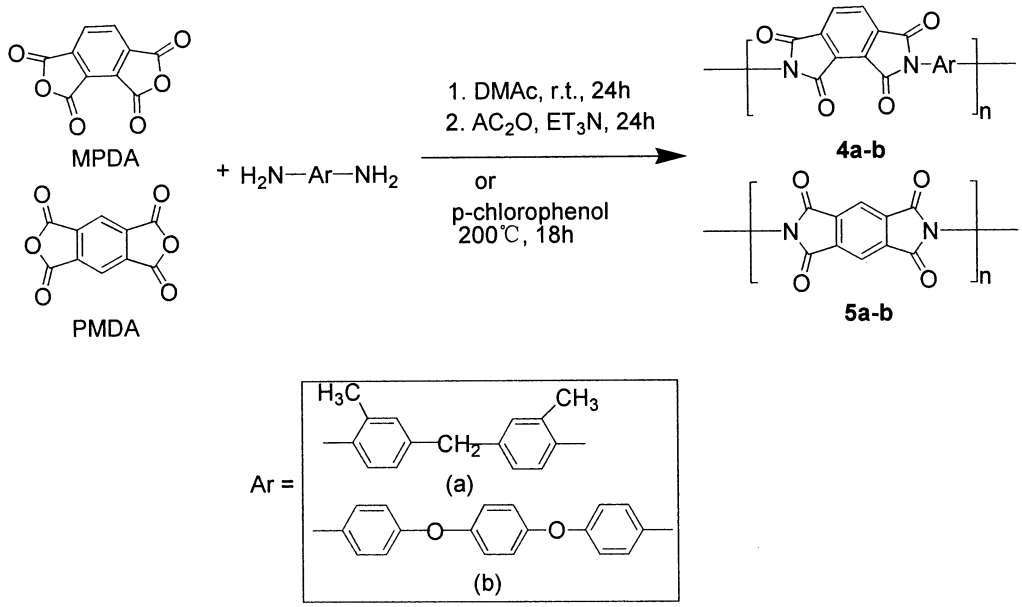
Inherent viscosities of these polymers were in the range 0.78−1.78 dL/g. From IR spectra, the characteristic absorption bands of the imide ring appeared near 1780 (asym C═O stretching), 1720 (sym C═O stretching), 1380 (C−N stretching), and 725 cm^{-1} (imide ring deformation), indicating polymers had been fully imidized. The T_g of polyimides **4a** and **4b** were 354 and 292 °C, respectively, higher than the corresponding PMDA-based polyimides **5a** (274 °C) and **5b** (272 °C). Evidently, the increase of T_g is attributed to the strained rotation about the C−N bond in the polyimides derived from MPDA. The onset temperature for 5% weight loss for these isomeric polyimides was above 482 °C in nitrogen. The solution-cast films for polymers **4a** and **5a** were clear, flexible, and tough. WAXD showed that all these polyimides are amorphous (Figure 9).

The solubilities of the isomeric polyimides are shown in Table 3, unlike the behavior of other isomeric polyimides, which showed more soluble for the polyimides based on 3,4′- and 3,3′-linked dianhydrides than the corresponding polyimides from 4,4′-linked dianhy-

Scheme 9. Possible Reactions in Thermal Imidization of Amic Acid Derived from MPDA and Aniline in DMAc



Scheme 10. Synthesis of Polyimides



drides;[13,14] the polyimides based on MPDA and PMDA exhibit similar solubility.

Conclusions

Some diamines, such as 4,4′-oxydianiline and 4,4′-methylenedianiline, have a tendency to form cyclic oligomers with mellophanic dianhydride. The cyclic dimer from MPDA and MDA was obtained by solvent extraction and characterized by IR, NMR, MS, and single crystal X-ray analysis. The isomerism in the reaction of MPDA and amine was discussed. The 2,3-carbonyl groups are favorably amidized owing to the formation of cyclic adduct of hydrogen bond to the carbonyl group at the 3-position. A polymer with amide and carboxylic group linkage was obtained due to the presence of water in the conventional two-step procedure of preparation for polyimide. But the fully imidized polymer can be obtained by the one-step process in phenolic solvent at high temperature or chemical imidization using acetic anhydride and tertiary amine as dehydration agent. The polyimides based on MPDA and some diamines were prepared, and the thermal properties, mechanical properties, and solubilities in organic solvents were tested.

Acknowledgment. The authors express their thanks to the National Natural Science Foundation of China for financial support (No. 50033010, No. 20174040).

References and Notes

(1) There was some confusion about the nomenclature of 1,2,3,4-benzenetetracarboxylic acid and 1,2,3,5-benzenetetracarboxylic acid. In some papers (such as: Smith, L. I.; Byrkit, G. D. *J. Am. Chem. Soc.* **1933**, *55*, 4305. Smith, L. I.; Carlson,

E. J. *J. Am. Chem. Soc.* **1939**, *61*, 288. Wang, Z. Y.; Qi, Y. *Macromolecules* **1994**, *27*, 625) the authors suggested to follow the name of prehnitene of 1,2,3,4-tetramethylbenzene, named 1,2,3,4-benzenetetracarboxylic acid as prehnitic acid. In this article we would like to follow *Chemical Abstracts*; in this most popular source for chemical information, 1,2,3,4-benzenetetracarboxylic acid has been called mellophanic acid since 1927.

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(11) The procedure for the preparation of asymmetric dimethyl ester C(a) of mellophanic dianhydride was as follows: To a 50 mL round-bottomed flask fitted with a gas inlet, 3.00 g (13.75 mmol) of mellophanic dianhydride was slowly dissolved with gentle heating in 20 mL of dry methanol under dry nitrogen. After the reaction was complete to give a clear solution for 4 h, the methanol was removed under vacuum until crystallization was initiated. After overnight refrigeration, the crystals were filtered and dried under vacuum at 40 °C; 3.56 g (92%) of the pure dimethyl ester of mellophanic dianhydride was obtained, mp 134−135 °C. IR (KBr): 1733, 1695 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ (ppm) 13.77 (s, 2H), 8.05 (d, 1H), 7.95 (d, 1H), 3.84 (s, 3H), 3.76 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.56, 167.07, 166.33, 166.25, 133.66, 133.39, 132.95, 132.57, 131.34, 130.60. MS: Calcd for $C_{12}H_{10}O_8$ 282.38. Found $[M + H]^+$ 283.20. Elemental analysis: Calcd for $C_{12}H_{10}O_8$: C, 51.06; H, 3.55; O, 45.39%. Found: C, 50.88; H, 3.63; O, 45.49%.

(12) The procedure for the preparation of symmetric amic acid B(b) was as follows: To a 50 mL round-bottomed flask fitted with a gas inlet, 0.3890 g (2.09 mmol) of aniline (AN) and 12 mL of DMAc were added through nitrogen. After 0.4555 g (2.09 mmol) of MPDA was added to the flask over a period of 15 min, the reaction mixture was stirred for 6 h at room temperature. The resulting solution was poured into 100 mL of distilled water; the precipitate was filtered off, washed thoroughly with water, and dried under vacuum at 40 °C for 24 h. The yield was 0.74 g (97%); mp 166−167 °C. IR (KBr): 1710, 1660 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ (ppm) 13.43 (s, 1H), 10.26 (s, 1H), 8.07 (s, 1H) 7.01−7.53 (m, 5H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 169.66, 164.92, 139.34, 137.47, 132.64, 130.19, 128.54, 123.30, 119.64. MS: Calcd for $C_{22}H_{16}O_6N_2$ 404.38. Found $[M + H]^+$ 405.64. Elemental analysis: Calcd for $C_{22}H_{16}O_6N_2$: C, 65.35; H, 3.99; O, 23.73; N, 6.93%. Found: C, 64.90; H, 3.64; O, 24.24; N, 7.22%.

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