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Semicrystalline Polyimides Starting from AB-Type Monomers

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AB-type isomeric mixture of *m*- and *p*-monomethyl 4-(4′-aminophenoxy)phthalate (**I**) and its pure *m*-monomethyl ester isomer (**II**) were successfully synthesized from 4-nitrophenol and 4-nitrophthalonitrile. The polyimide was prepared via a two-step method in which the direct polycondensation reactions were carried out in *N*-methylpyrrolidone (NMP) in the presence of diphenyl(2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonate (DBOP) as a condensation agent. AB-type crystalline polyimides, with a glass transition temperature (T_g) of 260 °C, melting transition temperature (T_m) of 528 °C, and 10% weight loss temperature (T_{10}) of 575 °C, can be readily obtained by thermal imidization of poly(amic acid methyl ester) films. The polyimide films prepared by thermal imidization of the isomeric poly(amic acid methyl ester)s were tough, flexible, and transparent, whereas the film prepared from the pure *m*-monomethyl ester precursor was brittle and opaque, indicating that the constitutional isomerism of the precursors has a significant effect on the thermal imidization as well as properties of the resulting polyimide. Thermal imidization of the isomeric poly(amic acid methyl ester)s with different molecular weight resulted in polyimide films of essentially identical mechanical properties. X-ray diffraction measurements revealed that the polyimides had crystalline structure with a crystallinity of 20−31%.

Introduction

Aromatic polyimides have been widely used in aerospace, microelectronics, optoelectronics, and composites due to the combination of many desirable properties, such as excellent electrical and physical properties, superior wear, and chemical resistance, in addition to their high thermal and oxidative stability.[1−13] Since the appearance of polyimide on the market in the 1960s, many kinds of polyimides have been synthesized and studied in detail as a result of both commercial and scientific interests. The majority of these research studies have continuously concentrated on the AA−BB monomer systems, primarily because of the easy preparation and purification of these AA and BB monomers. By changing the combination of monomers, a variety of polyimides with a wide range of properties have been prepared. However, there are a few reports on the polyimides synthesized from AB-type monomers, such as amino(etheranhydride) and its derivatives,[14−18] as well as imidonitrophenols.[19,20] From a practical point of view, using AB-type monomers can avoid the strict stoichiometric control, which is required in AA−BB polycondensation systems, thereby offering advantages in the preparation and processing of this kind of material. So far, there is no report on the preparation of AB-type polyimide via the poly(amic acid alkyl ester) precursor method. This method remains the advantage in preparing polyimide both in film form and in powder form compared with the one-pot method.[16]

In this paper, an AB-type isomeric mixture of *m*- and *p*-monomethyl 4-(4′-aminophenoxy)phthalate (**I**) and its pure *m*-monomethyl 4-(4′-aminophenoxy)phthalate (**II**) were synthesized. Direct polycondensation of these two monomers and subsequent thermal imidization were

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investigated, as well as the thermal and mechanical properties of the resulting polyimide films.

Experimental Section

Materials. Commercially available 4-nitrophenol, 4-nitrophthalonitrile, and diphenyl(2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonate were purchased from Tokyo Kasei Organic Chemical Co. and used without further purification. Extra pure methanol from Nacalai Tesque Inc. was used without any purification. Dimethyl sulfoxide (DMSO) and *N*-methylpyrrolidone (NMP) were dried with calcium hydride overnight and then distilled under reduced pressure. Acetic anhydride was dried with magnesium, followed by distillation under nitrogen before use. Other reagents were used as received.

Monomer Synthesis. *4-(4′-Nitrophenoxy)phthalonitrile.* As 2.78 g (0.02 mol) of 4-nitrophenol was completely dissolved into 30 mL of methanol in a 200 mL flask, which was dried by using a heating gun under nitrogen, 1.08 g (0.02 mol) of sodium methoxide was added. The mixture was stirred at room temperature for 1 h. After removing the methanol by evaporation, 50 mL of dry DMSO and 3.46 g (0.02 mol) of 4-nitrophthalonitrile were added to the flask, followed by stirring at 60 °C for 6 h and 90 °C for 6 h. The resulting mixture was allowed to cool and was poured into 1 L of cold, dilute hydrochloric acid. The crude product was collected by filtration, washed with water, and dried in a vacuum. Recrystallization from benzene using activated charcoal afforded 3.6 g of 4-(4′-nitrophenoxy)phthalonitrile, yield 68%, mp 150−151 °C. ^{1}H NMR (DMSO-d_6, ppm): δ 8.30−8.33 (m, 2H), 8.17−8.20 (d, 1H), 7.99−8.00 (d, 1H), 7.63−7.66 (q, 1H), 7.36−7.40 (m, 2H). IR (KBr): 3078, 2234, 1612, 1604, 1583, 1516, 1485, 1346, 1309, 1252, 1215, 1165, 1086, 949, 864 cm^{-1}. Anal. Calcd for $C_{14}H_7N_3O_3$ (265.24): C, 63.39; H, 2.66; N, 15.85. Found: C, 64.01; H, 2.73; N, 16.10.

4-(4′-Nitrophenoxy)phthalic Acid. In a flask, 2.65 g (0.01 mol) of 4-(4′-nitrophenoxy)phthalonitrile and 26 mL of 85% phosphoric acid were stirred together at reflux for 2 h. After cooling to room temperature, the mixture was poured into 300 mL of cold, dilute aqueous potassium hydroxide. The mixture was stirred at room temperature for 6 h after modulating the pH value to 11, and then it was neutralized with 6 M hydrochloric acid to pH 3∼4, followed by stirring for 6 h. The product was collected by filtration and dried in a vacuum at room temperature. After recrystallization from aqueous acetic acid (15%), 2.2 g of 4-(4′-nitrophenoxy)phthalic acid was obtained, yield 83%, mp 167−169 °C. ^{1}H NMR (DMSO-d_6, ppm): δ 8.26−8.31 (m, 2H), 7.80−7.83 (q, 1H), 7.31−7.35 (q, 2H), 7.24−7.29 (m, 2H). IR (KBr): 3545, 3084, 1722, 1581, 1510, 1487, 1390, 1340, 1234, 1194, 1109, 1066, 949, 846 cm^{-1}. Anal. Calcd for $C_{14}H_9NO_7$ (303.24): C, 55.45; H, 3.00; N, 4.62. Found: C, 55.87; H, 2.98; N, 4.65.

4-(4′-Nitrophenoxy)phthalic Anhydride. A mixture of 3.03 g (0.01 mol) of 4-(4′-nitrophenoxy)phthalic acid, 10 mL (0.1 mol) of acetic anhydride and 20 mL of acetic acid were heated at reflux for 1 h, and then the acetic anhydride and acetic acid were completely evaporated under reduced pressure. Recrystallization of the residue from acetic anhydride gave 2.6 g of 4-(4′-nitrophenoxy)phthalic anhydride, yield 91%, mp 129−131 °C. ^{1}H NMR (DMSO-d_6, ppm): δ 8.31−8.34 (d, 2H), 8.13−8.16 (d, 1H), 7.69−7.75 (m, 2H), 7.34−7.37 (d, 2H). IR (KBr): 3074, 1850, 1778, 1587, 1479, 1348, 1277, 1234, 1109, 1076, 895, 740 cm^{-1}. Anal. Calcd for $C_{14}H_7NO_6$ (285.22): C, 58.95; H, 2.48; N, 4.91. Found: C, 59.20; H, 2.29; N, 4.86.

Monomethyl 4-(4′-Nitrophenoxy)phthalate. A mixture of 2.85 g (0.01 mol) of 4-(4′-nitrophenoxy)phthalic anhydride and 30 mL of methanol was heated at reflux for 30 min. After cooling, the resulting mixture was poured into 300 mL of ice/water. A 3.0 g amount of the isomeric mixture was collected by filtration, washed with cold water, and dried in a vacuum at room temperature, yield 95%. The isomer ratio was evaluated by ^{1}H NMR to be 2/1 (*m*-/*p*-monomethyl ester isomer, molar ratio). ^{1}H NMR (DMSO-d_6, ppm): δ 8.25−8.28 (m, 2H), 7.75−7.89 (q, 1H), 7.32−7.40 (m, 2H), 7.25−7.32 (m, 2H), 3.77−3.79 (d, 3H). IR (KBr): 3500, 3081, 1738, 1686, 1570, 1520, 1489, 1344, 1325, 1288, 1242, 1201, 1128, 1065, 983, 862 cm^{-1}. Anal. Calcd for $C_{15}H_{11}NO_7$ (317.27): C, 56.78; H, 3.50; N, 4.42. Found: C, 57.14; H, 3.23; N, 4.45.

A mixture of 2.85 g (0.01 mol) of 4-(4′-nitrophenoxy)phthalic anhydride and 30 mL of methanol was stirred at room temperature for 24 h. The resulting mixture was poured into 300 mL of ice/water. The crude product was collected by filtration, washed with cold water, and dried in a vacuum at room temperature. The isomer ratio was evaluated by ^{1}H NMR to be 85/15 (*m*-/*p*-monomethyl ester isomer, molar ratio). After twice recrystallization from a mixture of methanol and water, 2.1 g of *m*-monomethyl 4-(4′-nitrophenoxy)phthalate was obtained, yield 66%, mp 157−158 °C. ^{1}H NMR (DMSO-d_6, ppm): δ 8.28−8.31 (m, 2H), 7.90−7.93 (q, 1H), 7.36−7.40 (m, 2H), 7.27−7.30 (m, 2H), 3.77 (s, 3H). ^{13}C NMR (DMSO-d_6, ppm): δ 167.39, 166.81, 161.15, 157.21, 143.29, 135.77, 131.97, 127.34, 126.29, 121.41, 119.00, 118.83, 52.9. IR (KBr): 3490, 3075, 1736, 1682, 1607, 1587, 1574, 1525, 1489, 1442, 1344, 1288, 1238, 1161, 1070, 985, 851 cm^{-1}. Anal. Calcd for $C_{15}H_{11}NO_7$ (317.27): C, 56.78; H, 3.50; N, 4.42. Found: C, 56.94; H, 3.43; N, 4.41.

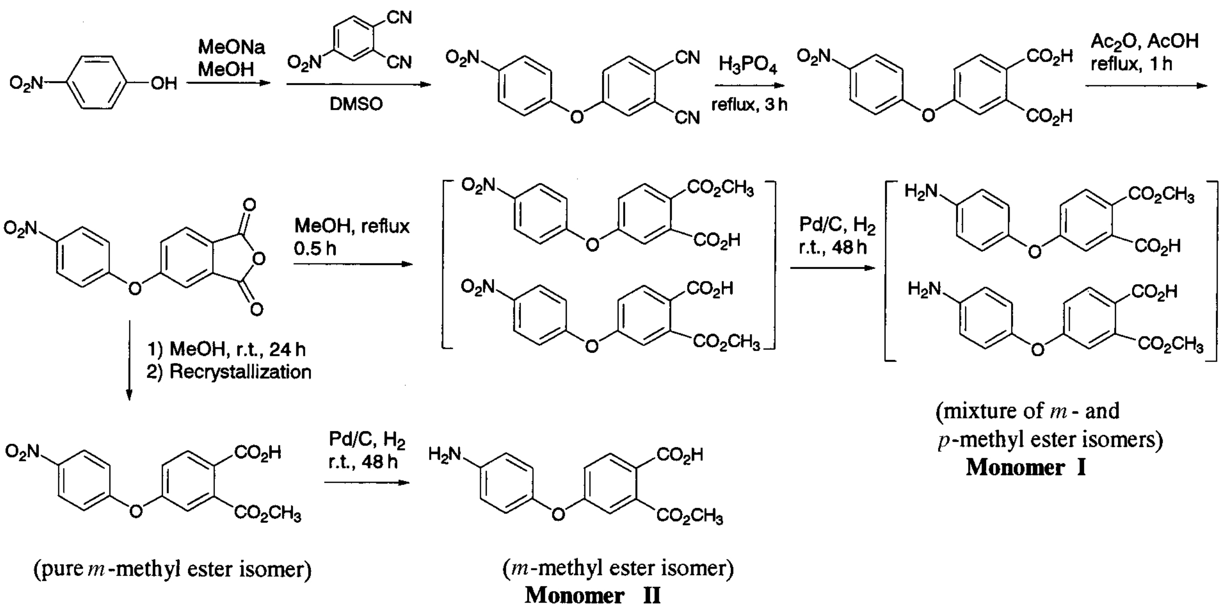
*Monomethyl 4-(4′-Aminophenoxy)phthalates **I** and **II**.* A mixture of 3.17 g (0.01 mol) of isomeric mixture monomethyl 4-(4′-nitrophenoxy)phthalate, 0.3 g of 10% palladium−charcoal catalyst, and 30 mL of methanol was stirred vigorously under hydrogen at room temperature for 48 h. The reaction mixture was filtrated with Celite to remove palladium−charcoal and washed with 300 mL of methanol. The filtrate was evaporated under reduced pressure and dried in a vacuum at 35 °C for 5 days. A 2.6 g amount of the isomeric mixture monomethyl 4-(4′-aminophenoxy)phthalate (**I**) was obtained with a yield of 91%. ^{1}H NMR (DMSO-d_6, ppm): δ 7.63−7.79 (q, 1H), 6.89−7.04 (m, 2H), 6.80−6.83 (m, 2H), 6.61−6.64 (m, 2H), 3.74−3.75 (d, 3H). IR (KBr): 3400, 2953, 2606, 1720, 1599, 1574, 1508, 1437, 1381, 1282, 1269, 1236, 1199, 1128, 1068, 981, 837, 787 cm^{-1}. Anal. Calcd for $C_{15}H_{13}NO_5$ (287.29): C, 62.71; H, 4.57; N, 4.88. Found: C, 63.06; H, 4.36; N, 4.77.

From the hydrogenation of *m*-monomethyl 4-(4′-nitrophenoxy)phthalate (3.17 g, 0.01 mol), 2.7 g of one isomer *m*-monomethyl 4-(4′-aminophenoxy)phthalate (**II**) was obtained with a yield of 94%, mp 77 °C (obtained from differential thermal analysis (DTA) curve). ^{1}H NMR (DMSO-d_6, ppm): δ 7.78−7.80 (d, 1H), 6.88 −7.04 (m, 2H), 6.81−6.84 (q, 2H), 6.61−6.64 (q, 2H), 3.74 (s, 3H). ^{13}C NMR (DMSO-d_6, ppm): δ 168.22, 166.80, 161.56, 146.40, 143.89, 135.84, 131.74, 123.76, 121.42, 117.31, 114.90, 114.53, 52.42. IR (KBr): 3450, 2951, 1721, 1664, 1601, 1541, 1506, 1479, 1439, 1379, 1277, 1240, 1215, 1088, 837 cm^{-1}. Anal. Calcd for $C_{15}H_{13}NO_5$ (287.29): C, 62.71; H, 4.57; N, 4.88. Found: C, 62.96; H, 4.46; N, 4.79.

Direct Polycondensation. A typical process: 0.317 g (1.1 mmol) of *m*-monomethyl 4-(4′-aminophenoxy)phthalate (**II**), 0.527 g (1.38 mmol) of DBOP, 0.15 mL of triethylamine (1.1 mmol) and 1.0 mL of NMP were added to a three-neck flask, which was dried with a heating gun in vacuum. The mixture was stirred at room temperature for 12 h under nitrogen, then diluted with NMP (4 mL), and poured into methanol (1 L) containing 0.1% lithium chloride. The polymer was collected and dried in a vacuum at 30 °C for 24 h. A 0.28 g amount of poly(amic acid *m*-methyl ester) (PAME) with the molecular weight of $1.94 \times 10^4 (M_n)$ and polydispersity of 2.3, was obtained, yield 94%. The inherent viscosity of the resulting polymer in NMP was 0.21 dL g^{-1} at a concentration of 0.5 g dL^{-1} at 30 °C. ^{1}H NMR (DMSO-d_6, ppm): δ 10.48−10.55 (m, amide H), 6.62−8.03 (m, ArH), 3.67−3.76 (m, $-OCH_3$). ^{13}C NMR (DMSO-d_6, ppm): δ 166.3, 166.0, 158.6, 150.5, 136.2, 132.2, 131.7, 130.2, 121.5, 120.4, 120.1, 117.2, 52.5.

Thermal Imidization of Cast Films of Poly(amic acid methyl ester)s. A 0.5 g amount of polyamic acid methyl ester was stirred with 2.0 mL of NMP overnight, and the mixture turned to clear solution. Film cast on the glass plate from the clear solution was put into a vacuum oven and kept 1 h each at room temperature, 100 °C, 200 °C, and 300 °C and then cooled to room temperature slowly.

Scheme 1



Characterization. Infrared (IR) spectra were recorded on a JASCO FTIR-8100 Fourier transform infrared spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-AL 300 MHz spectrometer. Thermogravimetric analysis (TGA) and differential thermal analyzer (DTA) were carried out with a Seiko TG/DTA 6200 at a heating rate of 10 °C/min under nitrogen. Differential scanning calorimetry (DSC) was performed on a Seiko DSC 6200 using a heating rate of 5 °C/min in nitrogen. Thermal mechanical analysis (TMA) was conducted on a Seiko TMA/SS6000 in a penetration mode with a load of 10 g and a heating rate of 5 °C/min. Dynamic mechanical thermal analysis (DMA) was performed on a dynamic mechanical analyzer DVA-200S in tension mode at a heating rate of 5 °C/min and a frequency of 10 Hz. Inherent viscosity of PAME was measured in NMP (0.5g dL^{-1}) at 30 °C. Gel permeation chromatography (GPC) was performed on a JASCO HPLC 880PU fitted with polystyrene–divinylbenzene columns (two Shodex KD806M and KD802) and a Shodex RI-71 refractive index detector in dimethylformamide (DMF) containing 0.01 M of lithium bromides as an eluent. Tensile tests were carried out on a TENSILON/UTM-II-20 machine with a strain rate of 4 mm/min at room temperature. The specimens for the test are in the size of 40 × 5 mm and the thickness of ca. 20 μm. Wide-angle X-ray diffraction (WAXD) was recorded with a Rigaku RU-200 diffractometer using Cu Kα radiation (50 KV, 180 mA, $\lambda = 0.154$ nm) with monochromator. The WAXD intensity was measured in the scattering angle range of 5–40° at a scanning speed of 1°/min.

Results and Discussion

Monomer Synthesis. The AB-type isomeric mixture of *m*- and *p*-monomethyl 4-(4′-aminophenoxy)phthalate (**I**) was synthesized by the hydrogenation of monomethyl 4-(4′-nitrophenoxy)phthalate, which was derived from the ring-opening reaction of the corresponding anhydride with methanol (Scheme 1). In general, aqueous potassium hydroxide–ethanol is used for the hydrolysis of substituted phthalonitrile to prepare dicarboxylic acids.[21–23] However, due to the presence of three strong electron-withdrawing groups, one nitro and two cyano groups, the ether bond in 4-(4′-nitrophenoxy)phthalonitrile would preferentially break rather than to hydrolyze the two cyano groups upon contact with aqueous potassium hydroxide–ethanol even at room temperature. When 4-(4′-nitrophenoxy)phthalonitrile was heated with 85% phosphoric acid,[24] the corresponding dicarboxylic acid was obtained in a yield of 83%.

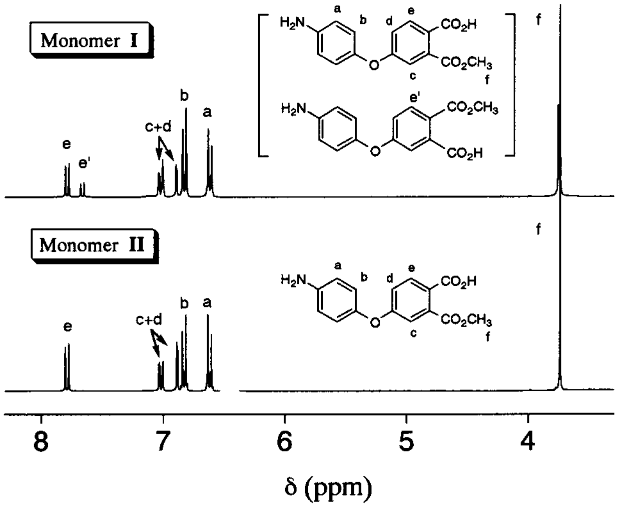


Figure 1. ^{1}H NMR spectra of the isomeric mixture **I** and pure *m*-methyl ester monomer **II**.

In the ring-opening reaction of 4-(4′-nitrophenoxy)phthalic anhydride with methanol, two isomers, *m*-methyl ester and *p*-methyl ester, were formed. The isomer ratio of the crude product was found to be influenced by the reaction temperature. As the ring-opening reaction of the anhydride was carried out at reflux temperature, the ratio of the *m*-/*p*-methyl esters was 2/1 (molar ratio), determined by ^{1}H NMR. The isomeric mixture was hydrogenated to form monomer **I** without separation of the isomers. On the other hand, *m*-methyl 4-(4′-nitrophenoxy)phthalate was the domi-

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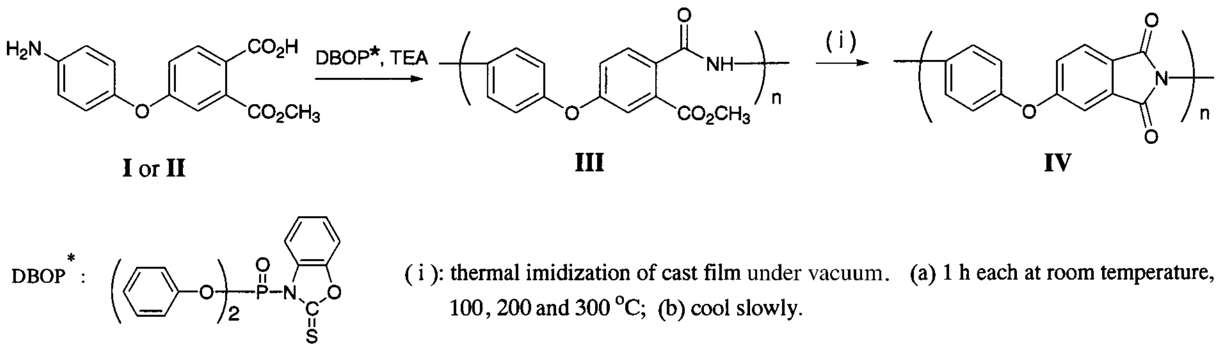
Scheme 2



(i): thermal imidization of cast film under vacuum. (a) 1 h each at room temperature, 100, 200 and 300 °C; (b) cool slowly.

Table 1. Results of Direct Polycondensation of Monomers I and II in NMP[a]

PAME	monomer	DBOP(g)	NMP (mL)	time (h)	yield (%)	η_{inh}[b] (dL g^{-1})	$\overline{Mw}$[c] (10^4)	$\overline{Mn}$[c] (10^4)	PDI[c]
III$_1$	**I**	1.54	3.0	24	97	0.34	8.58	3.60	2.4
III$_2$	**I**	1.54	6.0	1	80	0.22	5.09	2.20	2.3
III$_3$	**I**	1.11	12.0	6	70	0.16	2.91	1.56	1.9
III$_4$	**II**	1.54	3.0	24	93	0.24	4.98	2.60	1.9

[a] Direct polycondensation condition: monomer, 0.92 g (3.2 mmol); triethylamine (TEA), 0.45 mL (3.2 mmol), at room temperature. [b] Measured in NMP at 30 °C (0.5 g/100 mL). [c] Obtained by GPC with polystyrene calibration.

nant product when the ring-opening reaction was conducted at room temperature. Recrystallization of the crude product afforded the pure *m*-methyl 4-(4′-nitrophenoxy)phthalate. The purified product was hydrogenated to give pure *m*-methyl 4-(4′-aminophenoxy)phthalate **II**. The structures of monomers **I** and **II** were confirmed by ^{1}H NMR, ^{13}C NMR and elemental analyses. As shown in Figure 1, the isomer ratio of monomer **I** was determined by the integration of the proton **e** and **e′** to be 1:2 for the *p*- to *m*-methyl ester isomer. For monomer **II**, it can be observed that the peaks assigned to the proton **e′** (for the *p*-methyl ester isomer) entirely disappeared, showing the absence of the *p*-methyl ester isomer. In the ^{13}C NMR spectrum of monomer **II**, 13 kinds of carbons were observed, which is in agreement with its structure.

Direct Polycondensation To Form Poly(amic acid methyl ester)s. All polyimides were prepared by a two-step method outlined in Scheme 2. The direct polycondensation reactions of monomers I and **II** were carried out in NMP in the presence of diphenyl(2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonate (DBOP) and triethylamine.[25-27] The poly(amic acid methyl ester)s (**IIIs**) were obtained by pouring the reaction mixture into methanol containing 0.1% lithium chloride. The polycondensation results are shown in Table 1. Direct polycondensation of monomer **I** gave PAME (**III$_1$**) with a higher molecular weight and inherent viscosity than those of precursor **III$_4$** starting from monomer **II** at the same polymerization conditions. This is probably due to the relatively lower solubility of **III** prepared from the one structural monomer **II**. It was actually observed that the reaction mixture of the pure *m*-methyl ester monomer **II** turned heterogeneous during the reaction, whereas the polymerization of monomer **I** proceeded homogeneously. By changing reaction conditions, the amount of DBOP and NMP, and the reaction time, **IIIs** with different molecular weights were prepared from monomer **I**. The structure of **III** was confirmed by IR, ^{1}H NMR, and ^{13}C NMR measurements. In the IR spectra, a new absorption band attributed to amide carbonyl groups appeared at 1667 cm^{-1}, and the specific amide proton resonance appeared at ca. 10.5 ppm in the ^{1}H NMR spectra of **III**.

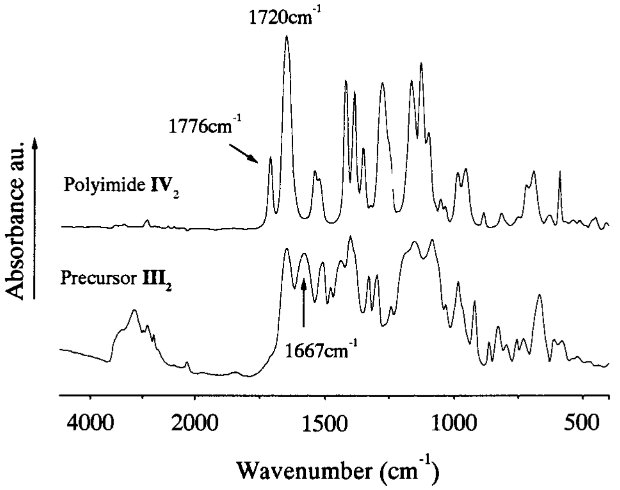


Figure 2. IR Spectra of polyimides and poly(amic acid methyl ester).

Thermal Imidization. These four precursor polymers (**IIIs**) were converted to polyimides by thermal imidization. Films of **III** were cast onto the glass plates from their NMP solutions. The films on the plates became opaque after 30 min at room temperature for the cases of **III$_1$**, **III$_2$**, and **III$_3$**. On the other hand, significant phase separation was observed in 30 min for the film from **III$_4$**. All films were placed into a vacuum oven as cast and kept for 1 h each at room temperature, 100 °C, 200 °C, and 300 °C. In the IR spectra of the resulting polyimide films, as shown in Figure 2, the characteristic absorptions assigned to imide carbonyl groups were observed at 1776 and 1720 cm^{-1}, while the amide absorptions at 1667 and 3300 cm^{-1} disappeared entirely, indicating the completion of thermal imidization.

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Table 2. Thermal and Mechanical Properties of Resulting Polyimide Films

PI	PAME	T_g[a] (°C)	T_s[b] (°C)	T_g[c] from $E'/E''/(\tan\delta)$	T_m[d] (°C)	T_2/T_{10}[e] (°C)	char[f] (%)	strength[h] (Mpa)	elong.[i] (%)	modulus[j] (Gpa)
IV$_1$	**III**$_1$	266	275	276/294/308	526	541/577	58	223	8	4.65
IV$_2$	**III**$_2$	261	273	276/296/307	528	538/575	59	208	8	4.24
IV$_3$	**III**$_3$	260	286	288/308/314	506	489/528	57	213	8	4.37
IV$_4$	**III**$_4$	260	–	–	508	507/575	59	–	–	–

[a] From the first heating scan under nitrogen, heating rate, 5 °C/min. [b] Obtained by TMA measurement at a heating rate of 5 °C/min. [c] The glass transition temperature obtained from DMA measurement. [d] Melting temperature obtained from DTA curves. [e] Temperature at which 2% (T_2) and 10% (T_{10}) weight loss recorded by thermogravimetry at a heating rate of 10 °C/min. [f] Residue weight % at 800 °C in nitrogen. [h] Load at break. [i] Elongation at break point. [j] Initial modulus.

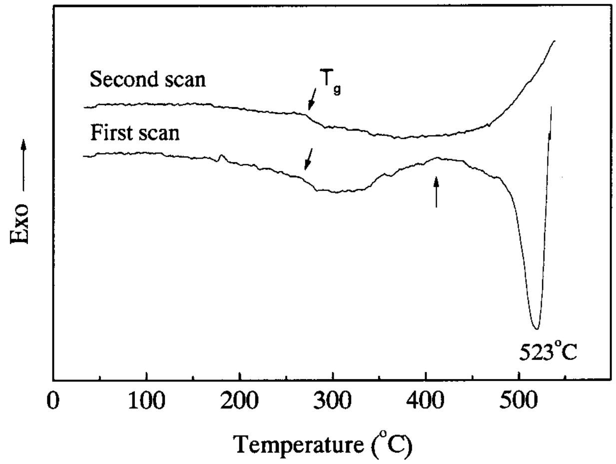

Figure 3. DSC curves of polyimide **IV**$_2$.

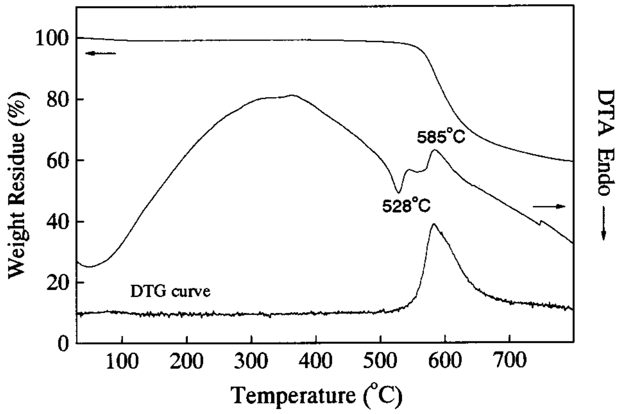

Figure 4. TGA/DTA curves of polyimide **IV**$_2$.

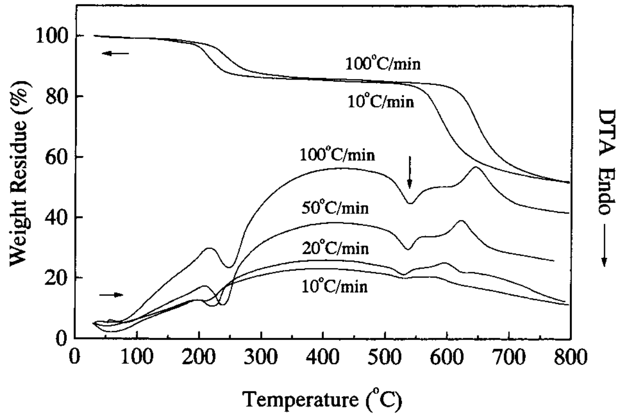

Figure 5. TGA/DTA curves of precursor **III**$_2$ at different heating rates.

Interestingly, the thermal imidization of the isomeric precursors **III**$_1$, **III**$_2$, and **III**$_3$ resulted in flexible and almost transparent films; however, the thermal imidization of the pure meta-precursor **III**$_4$ resulted in a brittle and opaque polyimide.

Thermal and Mechanical Properties. Thermal and mechanical properties of the resultant polyimide films were evaluated by TGA/DTA, DSC, and DMA measurements. The results are summarized in Table 2.

A typical DSC thermogram of the resultant polyimide film **IV**$_2$ is provided in Figure 3. The first heating scan showed a glass transition temperature at 260 °C and then a broad exotherm related to cold crystallization. Finally, a prominent endotherm, which is related to the melting transition and probably accompanied with little decomposition, was observed at 523 °C. As the temperature reached 530 °C, the sample was quenched to room temperature, and the second scan was carried out. The glass transition was also observed on the second scan at 270 °C. However, no obvious exotherm and endotherm related to crystallization and melting transition were observed prior to the final decomposition. This is probably because the DSC's first scan to 530 °C (about 1% weight loss in TGA curve at this temperature) resulted in some decomposition and consequently hindered the crystallization of polyimide on the second scan.

Figure 4 shows typical TGA/DTA curves of the resulting polyimide films. It is clear that this polyimide exhibited excellent thermal stability, since no obvious weight loss was found on the differential thermogravimetric (DTG) curve below 500 °C. On the DTA curve, an endotherm at 528 °C associated with the melting transition of the crystalline polyimide was clearly observed. This is followed by an exotherm attributed to the decomposition of the material. Looking back to the TGA/DTA curves of precursor **III**$_2$ at different heating rates (Figure 5), an obvious endotherm associated with melting transition of crystalline polyimide was also observed at about 530 °C, even when the heating rate was 100 °C/min. This indicated that crystallization of the polyimide occurred rapidly during the thermal imidization of precursor **III**, and semicrystalline polyimide can be readily obtained.

From DMA measurements (Figure 6), the polyimide films exhibited some retention of storage modulus above its glass transition temperature, indicating the presence of crystalline structures. The storage and loss modulus as well as the glass transition temperature of polyimide film on the second scan was higher than those on the first scan. This might be attributed to cold crystallization during the heating scan.

Young's modulus, stress at break and elongation of polyimide films determined by tensile tests are also

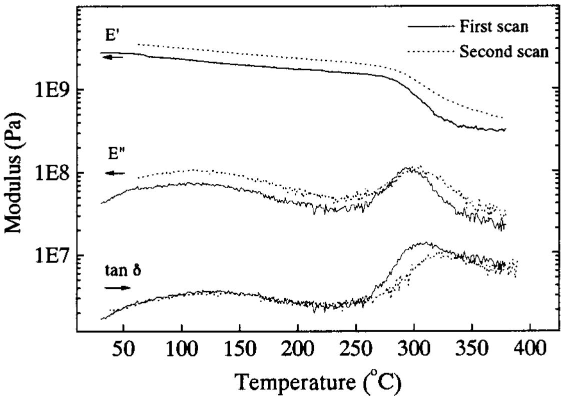

Figure 6. DMA curves of polyimide $\mathbf{IV}_2$.

listed in Table 2. Mechanical properties of the flexible polyimide films prepared from the precursors ($\mathbf{III}_1$, $\mathbf{III}_2$, and $\mathbf{III}_3$) with different molecular weights ($M_n = 3.6 \times 10^4$, 2.2×10^4, and 1.56×10^4) were essentially identical. For AA–BB systems, it has been demonstrated that the molecular weight of the final polyimide is nearly identical to its precursor poly(amic acid),[28,29] indicating that no obvious changes associated with branching, cross-linking, and/or chain extension occurred during the thermal imidization process. According to the results of the mechanical properties listed in Table 2, chain extension presumably occurred during the thermal imidization process of AB-type precursor polymers, which can be considered not only as the polyimide precursor but also as a macromonomer with an amino and a monomethyl phthalate end group. In addition to that, cross-linking could occur during the thermal imidization process. It is also possible that $\mathbf{III}_3$ had an excess of molecular weight over the limit, which is required to achieve mechanical properties for the resulting polyimide. However, it is difficult to determine the molecular weight of the resulting polyimide because of its insolubility in organic solvents.

Constitutional Isomerism. In general, AA–BB-type aromatic polyimides are prepared via a two-step method in which the first step, nucleophilic reaction on dianhydride carbonyls, actually results in poly(amic acid)s with several repeating units. It has been reported that the isomerism of the repeating units has an effect on the imidization behavior of the precursors, and the properties of the resulting polyimides.[30–33] However, there is no report concerning the isomerism effect of the AB-type precursor on its imidization and the properties of the resulting polyimide. For the present AB-type system, the precursor polymers ($\mathbf{III}_1$, $\mathbf{III}_2$, and $\mathbf{III}_3$) are actually copolymers with one-third *p*-methyl ester and two-thirds *m*-methyl ester repeating units, while $\mathbf{III}_4$ has only the *m*-methyl ester repeating unit. Although both isomeric precursor and pure meta-precursor give the same polyimide after imidization, the two kinds of precursors should have a different chain mobility and degree of crystallization behavior. Precursor $\mathbf{III}_4$ was easy to crystallize as solvent cast onto the glass plate. During thermal imidization, the polyimide resulted from $\mathbf{III}_4$ favors crystallization more than those from the isomeric precursors, giving rise to brittle polyimide.

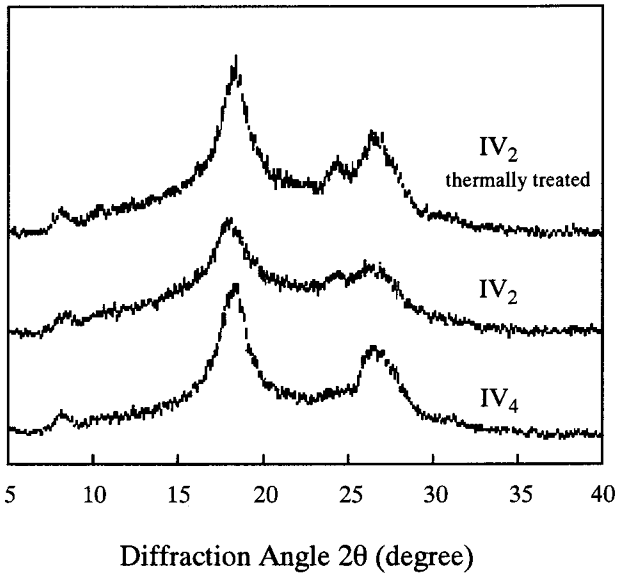

Figure 7. X-ray diffraction patterns of polyimides $\mathbf{IV}_2$, $\mathbf{IV}_4$, and $\mathbf{IV}_2$ heated to 480 °C at a heating rate of 20 °C/min and then cooled to room temperature.

Figure 7 shows the X-ray diffraction patterns of the polyimides $\mathbf{IV}_2$, $\mathbf{IV}_4$, and $\mathbf{IV}_2$ thermally treated at a heating rate of 20 °C/min to 480 °C. Clearly, both $\mathbf{IV}_2$ and $\mathbf{IV}_4$ contain crystalline structures, and the crystallinities were estimated to be 20% for $\mathbf{IV}_2$ and 31% for $\mathbf{IV}_4$, respectively. The main diffraction peaks were found at $2\theta = 8.1$, 18.3, 24.3, and 26.8° corresponding to *d*-spaces of 10.90, 4.84, 3.66, and 3.32 Å, respectively. As expected, the crystallinity of $\mathbf{IV}_4$ was higher than that of $\mathbf{IV}_2$. After thermal treatment, the crystallinity of $\mathbf{IV}_2$ was increased to 27%, close to that of $\mathbf{IV}_4$, and the film was still tough and flexible.

It is well-known that the physical and mechanical properties of a crystalline polymer are considerably dependent upon several factors, such as crystallinity, size, dimension, and distribution of crystallites as well as molecular arrangement. During thermal imidization, the pure meta-precursor was favorable to give polyimide with higher crystallinity in comparison with the isomeric precursor. Therefore, the brittleness in nature of $\mathbf{IV}_4$ was generated not only from its higher crystallinity but also from other factors, such as the size and distribution of its crystallites and molecular arrangement.

Conclusion

An isomeric mixture of *m*- and *p*-monomethyl 4-(4′-aminophenoxy)phthalate (**I**) as well as the one isomer *m*-monomethyl 4-(4′-aminophenoxy)phthalate (**II**) was successfully synthesized as AB-type monomers. Direct polycondensation reactions of the AB-type monomers, **I** and **II**, were carried out in NMP using DBOP as a

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condensation agent in the presence of triethylamine. The precursor polyamic acid esters (**III**s) were readily converted to the final polyimide by thermal imidization. The resulting polyimides were insoluble in organic solvents. Imidization of **III** prepared from **I** afforded tough, flexible and transparent polyimide films, whereas the case of monomer **II** gave rise to brittle and opaque polyimide. This result shows that the constitutional isomerism of the precursor has a large effect on its degree of crystallization behavior and the thermal imidization as well as the properties of the resulting polyimides. On the other hand, from the pure meta-precursor, AB-type polyimide with higher crystallinity can be obtained. Thermal and mechanical properties of the resulting polyimides were also investigated. The crystallinities of the polyimide films were determined to be 20−31%. The glass transition temperature and melting transition temperature of this AB-type polyimide were first observed at 260 and 528 °C, respectively.

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