

# Synthesis and Properties of AB-Type Semicrystalline Polyimides Prepared From Polyamic Acid Alkyl Ester Precursors

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## Introduction

Aromatic polyimide is one of the most important high-performance polymers. Because of their excellent electrical, thermal, and high-temperature mechanical properties, aromatic polyimides have found many applications in advanced technologies.<sup>1</sup> Semicrystalline polyimides provide the further advantages of enhanced resistance to organic solvents and bases, retention of mechanical properties above their glass transition temperature, and high thermooxidative stability. Many attempts have focused on semicrystalline aromatic polyimides over recent years.<sup>2</sup> Melt processing is more desirable both in terms of cost and environmental friendliness, thus the synthesis of thermoplastic and thermally stable aromatic polyimides is of prime interest. The efficient approaches to lower the glass transition temperature and melting transition temperature have involved the addition of flexible ether and carbonyl linkages, as well as the introduction of meta-substituted aromatic rings.<sup>3</sup>

All commercial thermoplastic aromatic polyimides are produced from the AA/BB monomer systems. To our knowledge, there is currently no thermoplastic aromatic polyimide made from direct-polycondensation of AB-type monomers. From a practical point of view, using AB-type monomer to prepare thermoplastic aromatic polyimides can provide further advantages in the preparation and processing of this kind of materials, since the ratio of two functional groups, 'A' and 'B', is limited to one to one. 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.

In this paper, five novel AB-type isomeric mixtures, monomethyl 4-(4-aminophenoxy)phthalate (**I**<sub>1</sub>), monomethyl 4-(3-aminophenoxy)phthalate (**I**<sub>2</sub>), 4-(4-aminophenoxy)diphenyl ether-3',4'-dicarboxylic acid monoethyl ester (**I**<sub>3</sub>), 3-(4-aminophenoxy)diphenyl ether-3',4'-dicarboxylic acid monoethyl ester (**I**<sub>4</sub>) and 2-(4-aminophenoxy)diphenyl ether-3',4'-dicarboxylic acid monoethyl ester (**I**<sub>5</sub>). Direct polycondensation of these five monomers and subsequent thermal imidization were investigated, as well as the thermal and mechanical properties of the resulting polyimide films.

## Experimental

**Materials.** Commercially available 3-nitrophenol, 4-nitrophenol, hydroquinone, resocinol, catechol, 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 and ethanol from Nacalai Tesque Inc. were used without any purification. Dimethyl sulfoxide (DMSO) and N-methylpyrrolidone (NMP) were dried with calcium hydride over night 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. The preparation of the AB-type monomers was described elsewhere.<sup>4</sup>

**Direct Polycondensation.** A typical process: 0.317 g (1.1 mmol) of monomethyl 4-(4-aminophenoxy)phthalate (**I**<sub>1</sub>), 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 vacuum at 30 °C for 24 h. A 0.28 g amount of poly(amic acid methyl ester) (PAME<sub>1</sub>) was obtained, yield 94%.

**Thermal Imidization of Cast Films of Poly(amic acid methyl ester)s.** A 0.5 g amount of polyamic acid alkyl 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 one hour each at room temperature, 100, 200, and 300 °C and then cooled to room temperature slowly.

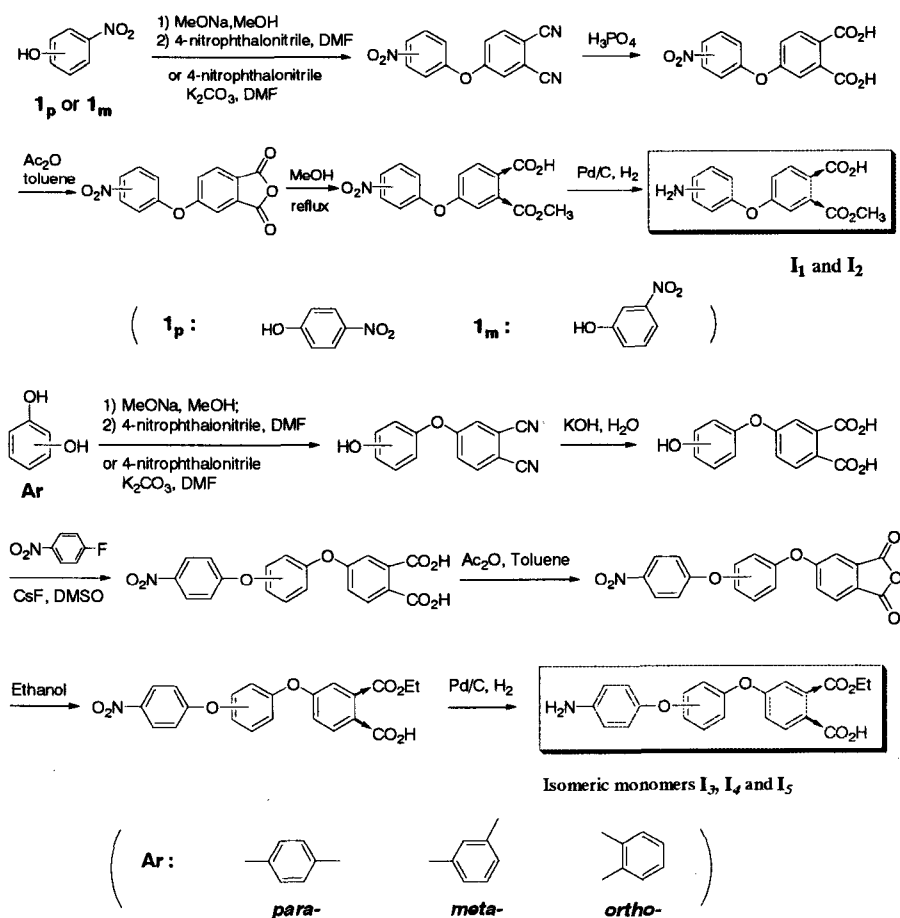
**Characterization.** Infrared (IR) spectra were recorded on a JASCO FTIR-8100 Fourier transform infrared spectrophotometer. <sup>1</sup>H NMR spectra were recorded on a JEOL JNM-AL 300 MHz spectrometer. Thermogravimetric analysis (TGA) and differential thermal analyzer (DTA) were carried out with a 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 10 °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<sup>-1</sup>) 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 bromide 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 x 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 (50KV, 180 mA, λ = 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 isomeric AB-type monomers, monomethyl 4-(4-aminophenoxy)phthalate (**I**<sub>1</sub>), monomethyl 4-(3-aminophenoxy)phthalate (**I**<sub>2</sub>), 4-(4-aminophenoxy)diphenyl ether-3',4'-dicarboxylic acid monoethyl ester (**I**<sub>3</sub>), 3-(4-aminophenoxy)diphenyl ether-3',4'-dicarboxylic acid monoethyl ester (**I**<sub>4</sub>) and 2-(4-aminophenoxy)diphenyl ether-3',4'-dicarboxylic acid monoethyl ester (**I**<sub>5</sub>) were successfully synthesized by hydrogenation of their corresponding nitro substituted compounds, which were prepared from the ring-opening reaction of the respective anhydrides with methanol or ethanol, as shown in Scheme 1. Generally, hydroquinone, resorcinol and catechol are used as a starting material to react with 4-nitrophthalonitrile or nitrofluorobenzene, followed by hydrolysis or hydrogenation to synthesize some symmetric dianhydrides or diamines, such as 1,2-bis(3,4-dicarboxyphenoxy)benzene dianhydride, 1,4-(4-aminophenoxy)benzene, 1,2-(4-aminophenoxy)benzene,<sup>5</sup> 1,3-bis(4-aminophenoxy)benzene. The nitro displacement reaction was applied in this paper to prepare the mono-substituted compounds, 4-(4-hydroxyphenoxy)phthalonitrile, 3-(4-hydroxyphenoxy)phthalonitrile, and 2-(4-hydroxyphenoxy)phthalonitrile with relatively higher yield of ca. 53% from hydroquinone, resorcinol and catechol, respectively.

Scheme 1



After hydrogenation, five novel AB-type monomers: **I**<sub>1</sub>, **I**<sub>2</sub>, **I**<sub>3</sub>, **I**<sub>4</sub>, and **I**<sub>5</sub>, were obtained in overall yields of ca. 30%. The structure of these monomers as well as the intermediates was confirmed by elemental analysis, infrared spectra (IR), and <sup>1</sup>H NMR spectra. The isomer ratios of these monomers calculated from the integration of the proton meta to the ether linkage were 2/1 (**I**<sub>1</sub>), 2/1 (**I**<sub>2</sub>), 7/3 (**I**<sub>3</sub>), 68/32 (**I**<sub>4</sub>), and 72/28 (**I**<sub>5</sub>) for meta-/para-methyl or ethyl ester isomer.

**Synthesis and Characterization of Poly(amic acid alkyl ester)s.** The AB-type polyimides were prepared by a two-step method. Direct polycondensation reactions of monomer **I**<sub>1</sub>, **I**<sub>2</sub>, **I**<sub>3</sub>, **I**<sub>4</sub>, and **I**<sub>5</sub> were carried out in the presence of diphenyl(2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonate (DBOP) and triethylamine. The results are presented in Table 1. The poly(amic acid methyl or ethyl esters)s PAME<sub>1</sub>, PAME<sub>2</sub>, PAEE<sub>3</sub>, PAEE<sub>4</sub> and PAEE<sub>5</sub> with relatively high molecular weights ( $M_n > 2.8 \times 10^4$ ) can be readily obtained in good yields under the polymerization conditions used, indicative of the sufficient purity of these AB-type monomers without further purification. The PAMEs and PAEEs exhibited good solubility in organic solvents, such as acetone, THF, DMF, DMSO, DMAc, NMP. The PAMEs and PAEEs obtained were characterized by IR and <sup>1</sup>H NMR spectra. The characteristic absorptions of amide groups were clearly observed at 1670 cm<sup>-1</sup> in the IR spectra of PAMEs and PAEEs, and the specific resonance at ca. 10.3 ppm in the <sup>1</sup>H NMR spectra of these precursors also supported the structures of poly(amic acid alkyl ester)s.

The thermal behaviors of these PAMEs and PAEEs were investigated by TG/DTA and DSC measurements. All the TG curves of PAMEs and PAEEs exhibited two-step drops at ca. 200 °C and 560 °C. The first and the second weight losses were associated with the elimination of methanol or ethanol generated by imidization and with the decomposition of resulting polyimides, respectively.

**Imidization of Poly(amic acid alkyl ester)s.** Five precursors were converted to the corresponding polyimides using thermal methods. The precursor solutions were cast onto the glass plates, and the plates were put into a vacuum oven, and kept for one hour each at room temperature, 100 °C, 200 °C and 300 °C. Five kinds of polyimide films PI<sub>1</sub>, PI<sub>2</sub>, PI<sub>3</sub>, PI<sub>4</sub> and PI<sub>5</sub> were obtained. The structure of the resulting polyimides was characterized by means of IR spectroscopy. IR spectra confirmed the completion of imidization process in thermal cyclodehydration. The characteristic absorption bands of the amide groups at around 3370 and 1667 cm<sup>-1</sup> disappeared, and those of the imide groups were clearly observed at 1778 cm<sup>-1</sup> (asym C=O str), 1720 cm<sup>-1</sup> (sym C=O str), 1390 cm<sup>-1</sup> (C-N str), 1100 and 745 cm<sup>-1</sup> (imide ring deformation).

**Table 1.** Results of Direct Polycondensation of Isomeric Monomers **I**<sub>1</sub>, **I**<sub>2</sub>, **I**<sub>3</sub>, **I**<sub>4</sub> and **I**<sub>5</sub>.

Polymer Code	Yield (%)	$\eta_{inh}^a$ (dL/g)	$M_w^b$ ( $10^4$ )	$M_n^b$ ( $10^4$ )	PDI <sup>b</sup>	$T_g^c$ (°C)	$T_i^d$ (°C)
PAME <sub>1</sub>	97	0.34	8.58	3.60	2.4	-	-
PAME <sub>2</sub>	91	0.28	6.41	2.83	2.3	-	-
PAEE <sub>3</sub>	93	0.31	8.00	3.52	2.3	159	203
PAEE <sub>4</sub>	94	0.40	14.48	5.00	2.9	141	210
PAEE <sub>5</sub>	90	0.31	8.46	4.14	2.0	147	215

<sup>a</sup>: measured in NMP at 30°C (0.5g/100ml); <sup>b</sup>: obtained by GPC with polystyrene calibration; <sup>c</sup>: determined from the first DSC heating scan; <sup>d</sup>: obtained from the peak value of imidization in DSC first scan.

**Properties of Polyimides.** The crystallinities of the polyimide films PI<sub>1</sub>, PI<sub>2</sub>, PI<sub>3</sub>, PI<sub>4</sub> and PI<sub>5</sub> were evaluated by wide-angle X-ray diffraction measurements. The diffraction patterns indicate that all the samples are semicrystalline polyimides except PI<sub>2</sub>. The crystallinity was estimated to be 20 % for PI<sub>1</sub>, 24 % for PI<sub>3</sub>, 21 % for PI<sub>4</sub> and 19 % for PI<sub>5</sub>, respectively. The main diffraction peaks were observed at 8.1, 18.3, 24.3, and 26.8° for PI<sub>1</sub>, 5.6, 17.5 and 18.4° for PI<sub>3</sub>, 5.8, 17.3 and 18.9° for PI<sub>4</sub>, 7.1, 14.4 and 17.4° for PI<sub>5</sub>.

The mechanical and thermal properties of the resulting polyimides were evaluated by tensile test, thermogravimetry (TG), differential scanning calorimetry (DSC), and dynamic mechanical analysis (DTA). The results are given in Table 2. The tensile strength, elongation at break, and initial modulus of these polyimide films were in the range of 98-235 Mpa, 8-21 %, and 1.9-4.5 Gpa, respectively. All polyimide films were tough and flexible, and exhibited larger tensile strength (195-231 Mpa) and elongation to break (15-21 %) except PI<sub>5</sub>. On the other hand, film PI<sub>5</sub> was relatively brittle, and it cracked before reaching its

glass transition temperature. All these polyimides exhibited good thermal stability up to 500 °C, and they had almost the same temperature of 5 % and 10 % weight loss at about 555 °C and 570 °C, respectively.

**Table 2.** Thermal and mechanical properties of AB-type polyimide films

Code	T <sub>g</sub> <sup>a</sup> (°C)	T <sub>s</sub> <sup>b</sup> (°C)	T <sub>g</sub> <sup>c</sup> (°C) from E'/E''/tgδ	T <sub>m</sub> <sup>d</sup> (°C)	ΔH <sub>f</sub> <sup>d</sup> (J/g)	T <sub>5</sub> /T <sub>10</sub> <sup>e</sup> (°C)	Char. <sup>f</sup> (%)	Stre. <sup>g</sup> (Mpa)	Elong. <sup>h</sup> (%)	Modulus <sup>i</sup> (Gpa)
PI <sub>1</sub>	266	275	276/296/307	528	-	541/577	58	235	8	4.5
PI <sub>2</sub>	215	-	238/247/261	-	-	531/558	57	231	15	2.8
PI <sub>3</sub>	216	210	218/231/242	373	26.6	507/526	52	195	15	2.1
PI <sub>4</sub>	176	175	189/193/202	333 337	16.8	558/570	55	231	21	2.3
PI <sub>5</sub>	181	182	170/171/171	321 328 337	13.5	534/556	51	98	8	1.9

<sup>a</sup>: From the second heating scan under nitrogen, heating rate, 5°C/min; <sup>b</sup>: Obtained by TMA measurement at a heating rate of 5°C/min; <sup>c</sup>: The glass transition temperature obtained from DMA measurement. <sup>d</sup>: Melting transition temperature and enthalpy obtained from DSC first scan; <sup>e</sup>: Temperature at which 5% (T<sub>5</sub>) and 10 % (T<sub>10</sub>) weight loss recorded by thermogravimetry at a heating rate of 10°C/min. <sup>f</sup>: Residue weight % at 800 °C in nitrogen. <sup>g</sup>: load at break; <sup>h</sup>: Elongation at break point; <sup>i</sup>: initial modulus.

## Conclusion

Five AB-type monomers (I<sub>1</sub>, I<sub>2</sub>, I<sub>3</sub>, I<sub>4</sub> and I<sub>5</sub>) were synthesized in this paper. The polyimides were prepared via a two-step method, in which the direct polycondensation reactions carried out in NMP using DBOP as a condensing agent gave poly(amic acid alkyl ester)s followed by thermal imidization to give the corresponding polyimides. The resultant polyimides were semicrystalline (except PI<sub>2</sub>) and exhibited good mechanical properties and thermal stability. The glass transition and melting transition temperatures were in the range of 176-266 °C and 308-528 °C, respectively. The crystallinities of the AB-type polyimides were estimated by means of X-ray diffraction measurements to be 19-24 %. DSC studies revealed that polyimide PI<sub>3</sub> based on hydroquinone crystallized much fast than those based on resorcinol and catechol. Polyimide PI<sub>1</sub> and PI<sub>3</sub> showed a single melting endotherm, while PI<sub>4</sub> and PI<sub>5</sub> exhibited bimodal melting behavior.

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