Synthesis of Alternating Aromatic Copolyimides

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Introduction. A great interest exists in aromatic polyimides owing to their excellent thermal stability and mechanical properties. Many heat-resistant polymers based on aromatic polyimides have already been commercialized, and much of the more recent work has been devoted to enhance their physical properties and improve processability.[1]

Aromatic polyimides are usually prepared by the condensation reaction between an aromatic tetracarboxylic dianhydride and an aromatic diamine. Depending on selection of a dianhydride–diamine pair, a wide variety of physical properties are conferred to a polyimide.[2] Extensive research has been conducted in the area of tailoring the physical properties of the final polyimide by changing the structure of monomers and thereby preparing polyimides suitable for a special application. However, this approach is often restricted because of difficulties in synthesizing new aromatic tetracarboxylic dianhydrides.

Copolymerization is an alternative method for modifying the polymer properties to meet the specific requirement. Several copolyimides were prepared by random copolymerization using either a diamine and two different dianhydrides or a dianhydride and two different diamines.[3-9] Block copolyimides were reported to be obtained by reaction of two amino group terminated polyamic acids with a dianhydride.[10] Recently it was also found that block copolyimides or random copolyimides were obtained when two different polyamic acids were blended and thermally imidized.[11]

In the present work, we developed a method for preparing strictly alternating copolyimides. To our knowledge, this is the first report on alternating aromatic copolyimides even though alternating copolyimides containing aliphatic spacers have been reported.[12]

Experimental Section. *N,N'*-Bis(4-aminophenyl)-2,5-(diisopropoxycarbonyl)benzene-1,4-dicarboxamide (PDPM). A solution of pyromellitic dianhydride (100.0 g, 0.458 mol) in isopropyl alcohol (400 mL) was refluxed for 1 h and then placed in a refrigerator overnight. Crystals were isolated by filtration and washed with hexane to give 2,5-(diisopropoxycarbonyl)terephthalic acid (69.8 g, 45% yield). To a solution of the acid (10.0 g, 0.030 mol) in tetrahydrofuran (100 mL) was added triethylamine (8.3 mL, 0.060 mol) and then ethyl chloroformate (5.7 mL, 0.060 mol) at −10 °C. The solution was stirred for 0.5 h at the same temperature and added dropwise to a solution of 1,4-phenylenediamine (10.0 g, 0.092 mol) in tetrahydrofuran (50 mL). The reaction mixture was stirred for 1 day at room temperature. Diethyl ether (50 mL) was added to the solution. Precipitates were isolated by filtration and washed with hot water (70 °C, 3 × 50 mL). The product was further purified by recrystallization from 1-methyl-2-pyrrolidinone to yield 7.9 g (51.5% yield).

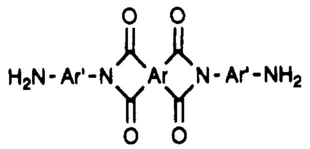
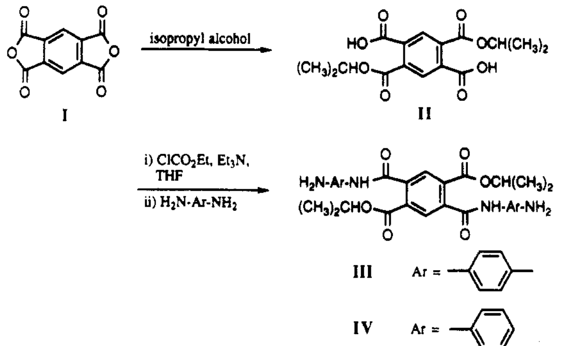
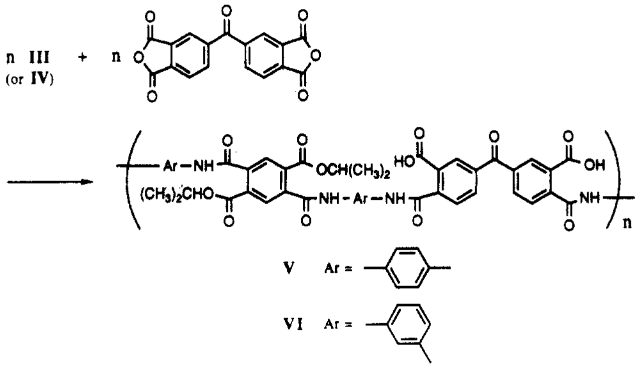


Figure 1. Structure of an aromatic imidodiamine.

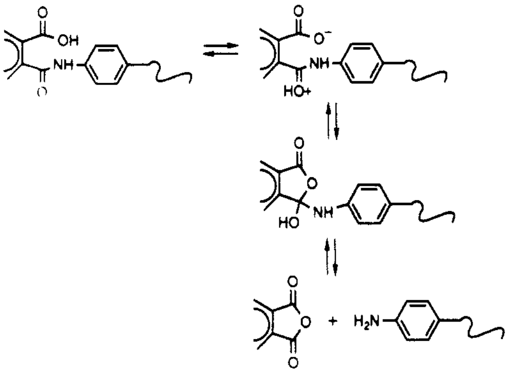
Scheme I



Scheme II



Scheme III



***N,N'*-Bis(3-aminophenyl)-2,5-(diisopropoxycarbonyl)benzene-1,4-dicarboxamide (MDPM).** This compound was prepared following a procedure for PDPM. The product was purified by recrystallization from ethanol–water. From 2,5-(diisopropoxycarbonyl)terephthalic acid (10.0 g, 0.030 mol) and 1,3-phenylenediamine (10.0 g, 0.092 mol) was obtained 7.5 g of the product (48.9% yield).

Polymerization. All polymerizations were carried out in 1-methyl-2-pyrrolidinone under nitrogen using stoichiometric amounts of diamines and dianhydrides. A typical procedure is as follows: To a solution of PDPM (1.0 g, 1.9 mmol) in 1-methyl-2-pyrrolidinone (18 mL) was added 3,3',4,4'-benzophenonetetracarboxylic dianhydride (0.62 g, 1.9 mmol) at 0 °C. After stirring for 2 h at room temperature, the solution was cast on a glass plate. The

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Scheme IV

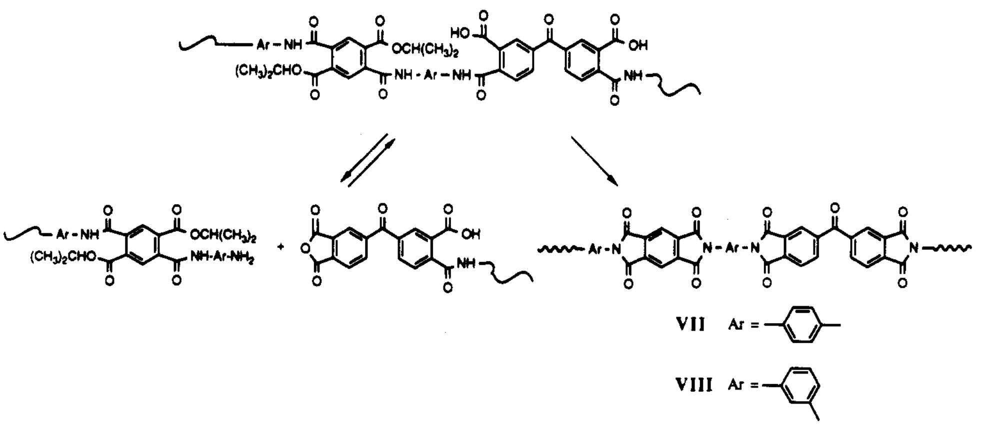

plate was heated for 1 h each at 80, 150, 250, and 350 °C under a flow of nitrogen, and the heating rate was 10 °C/min. The film was removed from the plate, washed with water and methanol, and dried in 1–2 mmHg at 100 °C for 10 h.

Results and Discussion. Alternating copolyimides could be prepared by using aromatic imidodiamines (Figure 1) and appropriate dianhydrides. However, such diamines usually show poor solubility in polymerization solvents; e.g., 1-methyl-2-pyrrolidinone and thus high molecular weight polymers are not obtained.[13] For this reason, we synthesized new diamines, which are soluble and easily converted into diimides with loss of alcohols upon heating (Scheme I).

The reaction of pyromellitic dianhydride with isopropyl alcohol produced a mixture of two isomers, i.e., 2,5-(diisopropoxycarbonyl)terephthalic acid and 4,6-(diisopropoxycarbonyl)isophthalic acid. ^{1}H NMR spectroscopy showed that the mixture contained two isomers in an equal amount.[14] They were separated by fractional recrystallization. The terephthalic acid isomer was readily crystallized out from an isopropyl alcohol solution. After removal of the terephthalic acid isomer by concentration and recrystallization, the isophthalic acid isomer was also obtained from the filtrate.

Direct amidation reaction of 2,5-(diisopropoxycarbonyl)-terephthalic acid with diamines was carried out by using ethyl chloroformate. A 50% excess of diamines was used. Formation of oligomers was not observed under the reaction conditions. This result was attributed to the fact that an amide group decreased the nucleophilicity of the second amino group. The diamines III and IV were characterized by elemental analysis and ^{1}H NMR spectroscopy.[15] The diamines III and IV did not show distinct melting points, probably due to reaction of the ester groups with the amide or amino groups.

Polymerization was carried out in 1-methyl-2-pyrrolidinone at room temperature using stoichiometric amounts of diamines and dianhydrides (Scheme II). Inherent viscosities of the polymer solutions were in a range of 0.5–1.2 dL/g. Without isolation of the resulting polymer, the solution was cast on a glass plate and the solvent was evaporated at 80 °C under a nitrogen flow. In the IR spectra of the films the characteristic band for imide groups at 1778 cm^{-1} appeared after initial drying and its intensity grew as the films were heated at elevated temperatures. The intensity of the C–H stretching band from isopropyl groups decreased very slowly compared to the intensity increase of the imide band at 1778 cm^{-1} until the films were heated above 200 °C, indicating that cyclization of the amide acid groups proceeded faster than that of the amide ester groups.

Table I
Glass Transition Temperatures of the Copolyimides and the Homopolyimides

		homopolymers[a]			
copolymers	T_g (°C)[b]	monomers	T_g (°C)[b]	monomers	T_g (°C)[b]
VII	360	PDA/PMDA[c]	>500	PDA/BTDA[c]	333
VIII	329	MDA/PMDA[c]	430	MDA/BTDA[c]	301

[a] The homopolymers were prepared from diamines and dianhydrides following the procedure for preparation of the copolyimides. [b] T_g's were determined by differential scanning calorimetric analyses. The heating rate was 10 °C/min. [c] PDA = 1,4-phenylenediamine, MDA = 1,3-phenylenediamine, PMDA = pyromellitic dianhydride, BTDA = 3,3′,4,4′-benzophenonetetracarboxylic dianhydride.

It is well-known that the amide acid units of poly(amic acids) are depolymerized to constituent anhydrides and diamines as shown in Scheme III.[11,16,17] Depolymerization is believed to proceed through an acid-catalyzed reequilibration reaction. This type of reaction was suppressed effectively by esterification of acid groups with appropriate alkyl groups.[18,19] Scheme IV describes the possible pathways for cyclization of polymers V and VI. Since depolymerization and recombination could occur at amide acid units but not at amide ester units, the polymers maintained their structures of alternating repeating unit sequences even after cyclization.

The copolyimides were not soluble in common organic solvents. In DSC analyses, they exhibited glass transition temperatures lower than the average value of the corresponding homopolyimides (Table I). The onset degradation temperatures of polymers VII and VIII obtained by thermal gravimetric analyses were 510 and 495 °C, respectively. Further characterization of the copolyimides and preparation of other alternating aromatic copolyimides are underway.

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References and Notes

(1) Wood, A. S. *Mod. Plast. Int.* **1989**, *June*, 26.
(2) Bessonov, M. I.; Koton, M. M.; Kudryavtsev, V. V.; Laius, L. A. *Polyimides: Thermally Stable Polymers*; Consultants Bureau: New York, 1987.
(3) Oishi, Y.; Itoyo, K.; Kakimoto, M.; Imai, Y. *Polym. J.* **1989**, *21*, 771.
(4) Lee, D. S.; Quin, G. *Polym. J.* **1989**, *21*, 751.
(5) Leung, L.; Williams, D. J.; Karasz, F. E.; MacKnight, W. J. *Polym. Bull.* **1980**, *16*, 457.
(6) Hedrick, J. L.; Labadie, J. W.; Palmer, T. D.; Russell, T. P. In *Polyimides: Materials, Chemistry and Characterization*; Feger, C., Khojastech, M., McGrath, J. E., Eds.; Elsevier: Amsterdam, 1989; p 61.

(7) Kawai, H.; Akahori, R.; Nagano, K. Jpn. Kokai Tokkyo Koho JP 01 16,834, 1989.

(8) Terauchi, M.; Ikeda, M.; Aritomi, M. Jpn. Kokai Tokkyo Koho JP 01 163,733, 1989.

(9) Kitahashi, M.; Yamamoto, Y.; Eto, S.; Fukami, A. Jpn. Kokai Tokkyo Koho JP 63 254,131, 1988.

(10) Suzuki, S.; Suzuki, T. Jpn. Kokai Tokkyo Koho JP 63 159,433, 1988.

(11) Ree, M.; Yoon, D. Y.; Volksen, W. *J. Polym. Sci., Part B: Polym. Phys.* **1991**, *29*, 1203.

(12) Avadhani, C. V.; Vernekar, S. P. *Polym. Bull.* **1990**, *24*, 487.

(13) Rhee, S. B.; Moon, B. S.; Park, J. W.; Chang, J. Y. Unpublished results.

(14) In the ^{1}H NMR spectrum of the mixture in acetone-d_6, the peak for aromatic protons of the terephthalic acid isomer appeared at 8.09 ppm, while the peaks for those of the isophthalic acid isomer appeared at 7.93 and 8.27 ppm.

(15) For compound III. Anal. Calcd: C, 64.85; H, 5.83; N, 10.80. Found: C, 64.76; H, 5.80; N, 10.70. ^{1}H NMR (DMSO-d_6): 10.19 (s, 2 H, CONH), 7.88 (s, 2 H, H3 and H6 of the tetrasubstituted benzene ring), 7.37 and 6.55 (2d, 8 H, Ar H2, H3, H4, and H5), 5.06 (m, 2 H, CH), 5.03 (s, 4 H, NH$_2$), 1.19 (d, 12 H, CH$_3$). For compound IV. Anal. Calcd: C, 64.85; H, 5.83; N, 10.80. Found: C, 64.75; H, 5.79; N, 10.65. ^{1}H NMR (DMSO-d_6): 10.21 (s, 2 H, CONH), 7.88 (s, 2 H, H3 and H6 of the tetrasubstituted benzene ring), 7.15–6.20 (m, 8 H, Ar H2, H4, H5, and H6), 5.05 (m, 6 H, CH and NH$_2$), 1.19 (d, 12 H, CH$_3$).

(16) Hasegawa, M.; Shindo, Y.; Sugimura, T.; Horie, K.; Yokota, R.; Mita, I. *J. Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 1515.

(17) Ree, M.; Yoon, D. Y.; Volksen, W. *Polym. Mater. Sci. Eng.* **1989**, *60*, 179.

(18) Nechayev, P. P.; Vygodskii, Y. S.; Zaikov, G. Y.; Vinogradova, S. V. *Polym. Sci. USSR* **1976**, *18*, 1903.

(19) Korshak, V. V.; Vinogradova, S. V.; Vygodskii, Y. S.; Gerashchenko, Z. V. *Polym. Sci. USSR* **1971**, *13*, 1341.