Synthesis of Rigid Alternating Copolyimides Containing a Bent Unit

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Rigid-rod aromatic poly(pyromellitimide)s are infusible and intractable materials with limited applications as thin films that are usually produced in two steps through thermal imidization of amic acid or amic ester precursors.[1] High solubility would warrant the one-step production of poly(pyromellitimide)s in bulk and facilitate the fabrication of a polyimide-based composite via a lamination process. The majority of methods used for improving the solubility while maintaining the high-temperature performance of polyimides have involved the structural modifications of dianhydride and diamine monomers.[2] Copolymerization of two different dianhydrides or two different diamines is also a common practice to improve the solubility and achieve a combination of desired properties.[3] To date, most of dianhydrides or diamines containing a flexible linkage such as ether, methylene, and hexafluoroisopropylidene groups are copolymerized in a random fashion.[3,4] Due to the disruption of symmetry and regularity of the polymer backbone, random copolyimides usually have the enhanced solubility. However, if two dianhydrides or two diamines have quite different reactivities, a short block of homopolymer may form first. Such oligoimides like oligo(*p*-phenylene pyromellitimide) may be insoluble in the polymerization solvent, which would prevent further chain growth. In fact, it is difficult to achieve a high content (ca. over 50%) of pyromellitimide by direct solution copolymerization of pyromellitic dianhydride (PMDA) and a dianhydride comonomer even with a flexible diamine such as 4,4′-oxydianiline or 4,4′-methylenedianiline.[3] It would be more difficult to obtain a high molecular weight soluble 1:1 copolyimide by direct random copolymerization of PMDA with another rigid dianhydride and stiff *p*-phenylenediamine. Nevertheless, the alternating copolyimides have recently been synthesized, although via amic ester precursors, from PMDA and 4,4′-(hexafluoroisopropylidene)diphthalic anhydride with *m*- and *p*-phenylenediamines.[5] Furthermore, the alternating copolyimides appeared to be more soluble than the corresponding random ones.

We previously reported the synthesis of a series of novel polyimides based on diphenylprehnitic dianhydride (**1**).[6] Among all soluble polyimides, the one without a bridging unit derived from **1** and *p*-phenylenediamine was notably soluble in *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMAc), 1,1,2,2-tetrachloroethane (TCE), and pyridine. Such remarkably high solubility can be attributed to the unique 122° bent functionality in dianhydride **1**.[6b] Subsequently, an attempt was made to render the soluble feature offered by **1** to rather insoluble rigid-rod poly(*p*-phenylene pyromellitimide) through random copolymerization.[7] The premature polymer precipitated from the reaction mixture of **1** and PMDA in 1:1 ratio with *p*-phenylenediamine in *m*-cresol. It was found that PMDA reacted faster than **1** to yield insoluble oligopyromellitimide. To improve the solubility by shortening the pyromellitimide blocks, the sequential addition was employed by first reacting *p*-phenylenediamine with **1** in 2:1 molar ratio and then slowly introducing PMDA. The resulting polymer remained soluble in *m*-cresol during polymerization but was still insoluble in TCE, DMAc, or *N*-methylpyrrolidinone (NMP).[7] Obviously, this sequential copolymerization could not produce the alternating copolyimide without defect or short block. Preston *et al.* have shown that using bent aromatic diamines derived from phthalic anhydride can improve the processability of stiff-chain polyimides.[2h] It is therefore appropriate to further investigate the effects of the absolute alternating structure and the bent prehnitimide unit that would have on the solubility of rigid copolyimides. We report here the one-step synthesis of perfectly alternating copolyimides from diamine **2** with PMDA and 1,4,5,8-naphthalenetetracarboxylic dianhydride (NDA), respectively.

The red-colored diamine **2** was synthesized by reduction of the dinitro precursor derived from **1** and 4-nitroaniline and fully characterized by spectroscopic means and chemical analysis.[8] The reduction could be done in moderate to high yields by hydrogenation with the PtO_2 catalyst. Polymerizations of diamine **2** with PMDA and NDA, respectively, were carried out in *m*-cresol in the presence of a small amount of isoquinoline at 200 °C. The solution concentration was best kept in 2% in order to prevent the gelation. Polyimides **3** and **4** (Figure 1) remained in solution during the course of polymerization.

Intrinsic viscosities of the "as-prepared" polyimides **3** and **4** were 0.57 and 0.89 dL/g (Table 1), relatively

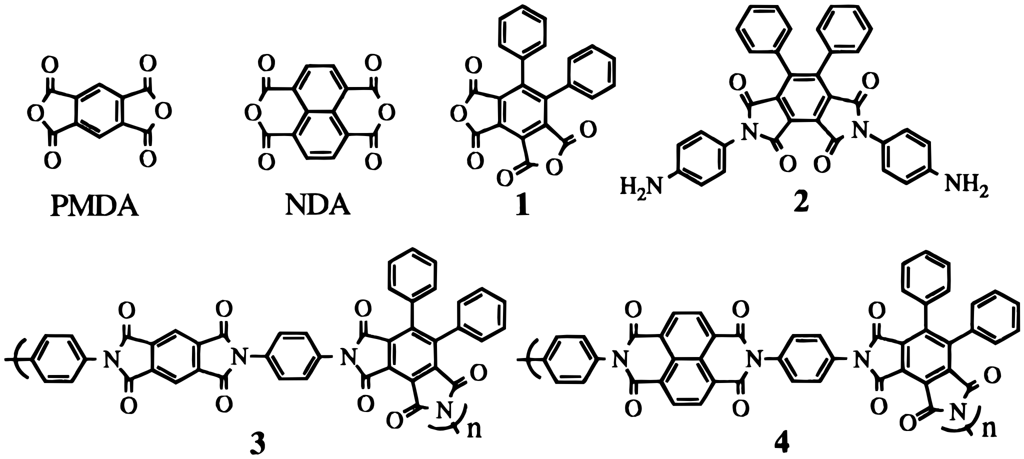

Figure 1. Diamine, dianhydrides, and alternating copolyimides.

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Table 1. Characteristics of Copolyimides 3 and 4

				solubility[d]					
polymer	viscosity (dL/g)[b]	T_d, °C in N$_2$[c]	T_d, °C in air[c]	TCE	DMF	DMAc	NMP	*m*-cresol	pyridine
3	0.57	365	356	−	+	+	+	+	+
3 (cured)[a]	1.04	530	424	−	+	±	+	+	±
4	0.89	505	403	+	+	+	+	+	+
4 (cured)	1.20	530	416	+	+	+	+	+	±

[a] Powdered "as-prepared" polyimides were heated at 300 °C for 10 min. [b] Intrinsic viscosity in NMP at 30 °C. [c] Onset temperature for 5% weight loss, obtained on a Seiko TG 220, at a heating rate of 10 °C/min. [d] Room temperature; Key: +, fully soluble; ±, partially soluble; −, insoluble.

lower than those for typical rigid-rod polyimides.[2a] But creasible tough films could be cast from the reaction solution for both polymers, indicating the formation of high molecular weight polymers. Relatively low viscosity can be attributed to the bent diimide structure and incomplete imidization. Thermogravimetry (TG) of both "as-prepared" polyimides showed the loss of water occurring at 280−300 °C. After being treated at 300 °C for a short time (10 min) to effect complete imidization, the powdered copolyimides showed no weight loss up to 450 °C. As expected, solution viscosities increased to 1.04 and 1.20 dL/g for **3** and **4**, respectively (Table 1).

The alternating diad structures of copolyimides **3** and **4** were confirmed by IR and NMR. To assist the characterization, three model bisimides **5**−**7** representing all three possible diads were prepared from *p*-phenylenediamine, phthalic anhydride, and 1,8-naphthalic anhydride.[9] Two characteristic carbonyl bands were observed for copolyimide **3** at 1730 and 1776 cm^{-1} in IR. Four carbonyl bands were found in the region of 1680−1775 cm^{-1} for **4**. Model imides **5**−**7** also showed those carbonyl bands in the same region.[9] The ^{1}H NMR spectrum of polymer **4** displayed two aromatic protons Ha and Hb from the *p*-phenylene moiety at 7.72 and 7.50 ppm. By comparing 2D-HETCOR spectra of model bisimides **5**−**7**, Ha and Hb were assigned to the protons adjacent to prehnitimido unit (at 7.72 ppm) and naphthalimido unit (at 7.50 ppm), respectively (spectrum a, Figure 2). For comparison, the corresponding two protons in bisimide **5** also appeared at 7.64 and 7.43 ppm (spectrum b, Figure 2). On the other hand, the same protons for the homopolyimide **8**[6] derived from **1** and *p*-phenylenediamine appeared as a singlet at 7.62 ppm, matching well to the corresponding proton peak of bisphthalimide **6** (7.59 ppm, spectra c and d). Furthermore, the phenylene protons of bisnaphthalimide **7** showed as a singlet at 7.47 ppm (spectrum e). In addition to the above corroborative data, the absence of two singles at 7.47 and 7.59 ppm in the spectrum (a) due to two symmetrical diads further proved the alternating structure of **4**.

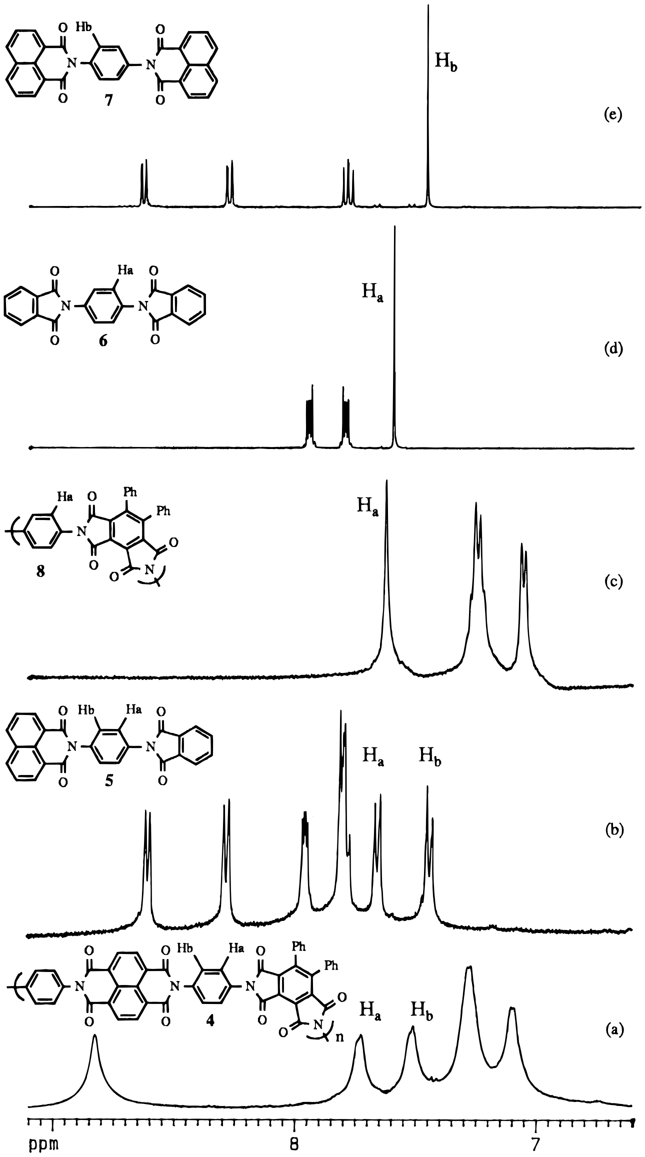

Figure 2. ^{1}H NMR (400 MHz, TCE-d_2) spectra of (a) copolyimide **4**, (b) bisimide **5**, (c) poly(*p*-phenylene diphenylprehnitimide) **8**, (d) bisphthalimide **6**, and (e) bisnaphthalimide **7**.

Alternating copolyimides **3** and **4** were remarkably soluble in organic solvents like DMF, DMAc, NMP, and *m*-cresol (Table 1). The significant improvement in solubility, as compared to the copolyimide produced by sequential copolymerization, is evidently attributed to the bent prehnitimide unit and the perfect alternate sequence. Regular insertion of the bent unit into the rigid-rod backbone effectively prevents the polymer chains from close packing or strong interchain interacting, thus allowing them to be solvated and dissolved. Pendant phenyl rings attached to the central benzene core also contribute to the diminution of strong interchain interaction to some extent. It is worthy to note that copolyimide **4** containing the naphthalimide moiety was more soluble than **3** in TCE. It was also noticed that the polymers became slightly less soluble after being thermally treated in the solid powder form. The minor decrease in solubility was primarily due to the completion of imidization, rather than the increase in crystallinity or cross-linking. Wide-angle X-ray diffractograms of "as-prepared" **4** showed a low degree of crystallinity. There was no sign of distinct higher order for the thermally treated **4** (Figure 3). Polymer **3** had similar wide-angle X-ray diffractograms.

Copolyimides **3** and **4** displayed good thermal stability, as assessed by TG. The onset temperatures for 5% weight loss in nitrogen were 530 °C for both polyimides

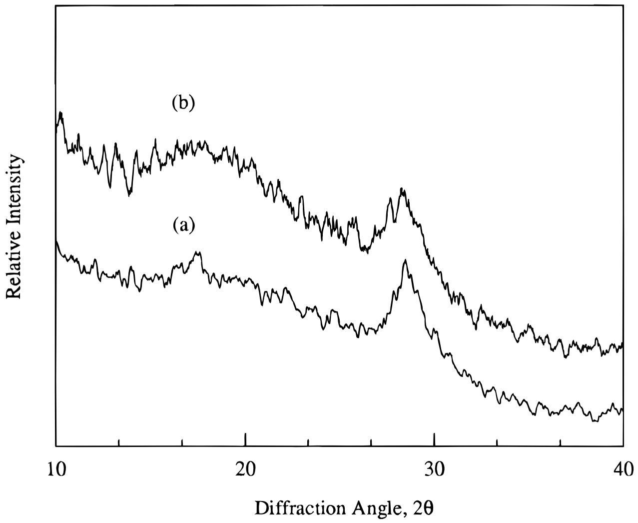

Figure 3. Wide-angle X-ray diffractograms of (a) "as-prepared" **4**, and (b) thermally treated **4**.

after thermal treatment. The "as-prepared" polyimides degraded easily in air, for the 5% weight loss occurring at 356 °C and 403 °C for **3** and **4**, respectively. Neither of the glass transition temperatures (T_gs) and crystalline melting endotherms was detected for **3** and **4** by differential scanning calorimetry. Young's moduli determined by thermomechanical analysis for both "as-prepared" polymers were in the vicinity of 3 GPa. After thermal treatment at 300 °C for 10 min, Young's modulus of polymer **4** dropped from 3.3 to 1.6 GPa. The decrease of Young's modulus is indicative of the increased stiffness of the polymer backbone as a result of further thermal imidization.

In conclusion, alternate insertion of a bent unit into the rigid-rod polyimide is an effective way to break the linear rod-like regularity and improve the solubility, as demonstrated by synthesizing soluble rigid polyimides **3** and **4**.

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References and Notes

(1) (a) Becker, K. H.; Schmidt, H.-W. *ACS Div. Polym. Mater. Sci. Eng. Proc.* **1992**, *66*, 303. (b) Yang, H. H. *Aromatic High Strength Fibers*; Wiley: New York, 1989; Chapter 6, pp 673–795.

(2) For selected examples: see (a) Harris, F. W.; Hsu, S. L. C. *High Perform. Polym.* **1989**, *1*, 3. (b) Giesa, R.; Keller, U.; Eiselt, P.; Schmidt, H.-W. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 141. (c) Tomikawa, M.; Cheng, S. Z. D.; Harris, F. W. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1995**, *36*(1), 707. (d) Matsuura, T.; Ishizawa, M.; Hasuda, Y.; Nishi, S. *Macromolecules* **1992**, *25*, 3540. (e) Harris, F. W.; Hsu, S. L. C.; Tso, C. C. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1990**, *31*(1), 342. (f) Matsuura, T.; Hasuda, Y.; Nishi, S.; Yamada, N. *Macromolecules* **1991**, *24*, 5001. (g) Matsuura, T.; Yamada, N.; Nishi, S.; Hasuda, Y. *Macromolecules* **1993**, *26*, 419. (h) Preston, J.; Carson, J. W., Jr. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1992**, *33*(1), 390.

(3) Harris, F. W.; Lanier, L. H. In *Structure-Solubility Relationships in Polymers*; Harris, F. W., Seymour, R. B., Eds., Academic Press: New York, 1977; p 183.

(4) Hedrick, J. L.; Labadie, J. W.; Palmer, T. D.; Russell, T. B. In *Polyimides: Materials, Chemistry and Characterization*; Ferger, C., Khojastech, M., McGrath, J. E., Eds.; Elsevier: Amsterdam, 1989; p 61.

(5) (a) Rhee, S. B.; Park, J. W.; Moon, B. S.; Chang, J. Y. *Macromolecules* **1993**, *26*, 404. (b) Park, J. W.; Lee, M.; Lee, M.-H.; Liu, J. W.; Kim, S.D.; Chang, J. Y.; Rhee, S. B. *Macromolecules* **1994**, *27*, 3459.

(6) (a) Wang, Z. Y.; Qi, Y. *Macromolecules* **1994**, *27*, 625. (b) Wang, Z. Y.; Qi, Y. *Macromolecules* **1995**, *28*, 4207.

(7) Wang, Z. Y.; Qi, Y. In *The Polymeric Materials Encyclopedia: Synthesis, Properties, and Applications*; Salamone, J. C., Ed.; CRC Press Inc.: Boca Raton, FL, in press.

(8) The solution of dianhydride **1** (17.0 g, 45.9 mmol) and 4-nitroaniline (15.8 g, 114.9 mmol) in *m*-cresol (30 mL) and isoquinoline (15 drops) was stirred under nitrogen at 170 °C for 6 h and then poured into 200 mL of 95% ethanol. The dinitro product was filtered and dried in air: 19.5 g (69.6%); mp 314 °C (DSC); IR (KBr, C=O), 1779, 1735 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (4 H, d, J = 9.08 Hz), 7.74 (4 H, d, J = 9.08 Hz), 7.30 (6 H, m), 7.09 (4 H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.96, 161.59, 148.24, 146.79, 136.74, 133.47, 132.61, 129.47, 128.96, 127.93, 127.65, 126.61, 124.38. The above dinitro compound (5.0 g) in tetrahydrofuran (45 mL) and 95% ethanol (20 mL) was reduced using PtO_2 (0.1 g) in a hydrogenation apparatus under 50 psi of hydrogen for 8 h at room temperature. After removal of the catalyst and solvents, diamine **2** was recrystallized from acetonitrile and dried in a vacuum oven at 150 °C overnight: 3.6 g (80%); mp 375 °C (DSC); IR (KBr, C=O) 1770, 1722 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.16 (10 H, m); 7.00 (4 H, d, J = 8.60 Hz); 6.62 (4 H, d, J = 8.60 Hz); 5.39 (4 H, s); ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.33, 163.01, 148.83, 144.73, 133.82, 133.39, 129.67, 128.10, 127.64, 127.43, 127.07, 119.31, 113.39. Anal. Calcd for $C_{34}H_{22}N_4O_4$, C 74.17%, H 4.03%, N 10.18%. Found: C 74.11%, H 3.92%, N 10.01%.

(9) Bisimide **5** was prepared from *N*-(4-aminophenyl)phthalimide and 1,8-naphthalic anhydride in *m*-cresol containing a few drops of isoquinoline at 200 °C. The former was synthesized by the reduction of *N*-(4-nitrophenyl)phthalimide with iron powders in acid aqueous tetrahydrofuran at 80 °C. Symmetric bisimides **6** and **7** were synthesized by heating *p*-phenylenediamine with phthalic anhydride and 1.8-naphthalic anhydride in 1-cyclohexyl-2-pyrrolidinone at 200 °C for 4 h, respectively. **5**: mp 344 °C (DSC); IR (KBr, C=O) 1779, 1720, 1705, 1668 cm^{-1}; MS (EI, *m/e*, relative intensity %) 418 ($M^{\bullet +}$, 89). **6**: mp 370 °C (DSC); IR (KBr, C=O) 1702, 1779 cm^{-1}; MS (EI, *m/e*, relative intensity %) 368 ($M^{\bullet +}$, 100). **7**: mp 332 °C (DSC); IR (KBr, C=O) 1705, 1665 cm^{-1}; MS (EI, *m/e*, relative intensity %) 468 ($M^{\bullet +}$, 58).

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