

Synthesis and Characterization of Aromatic Dianhydrides Containing Imide Precursor Units

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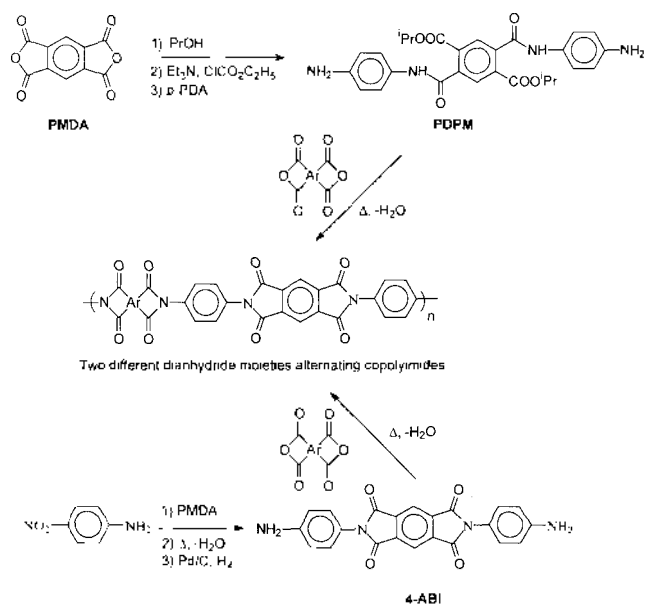
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Aromatic polyimides are known as one of the most important classes of high temperature polymers, and widely used in various industrial applications.¹⁻⁴ Polyimides are conventionally prepared by the thermal imidization of poly(amic acids), which are prepared by the reaction of dianhydrides and diamines. Since the chemical structures of dianhydrides and diamines critically affect the properties of polyimides, syntheses of new dianhydrides and diamines are very important to the development of new polyimides.

There are, however, only a limited number of ways to synthesize new monomers. In previous studies, Park *et al.* reported⁵ the synthesis of new diamine, *N,N*-bis(4-aminophenyl)-2,5-bis[(isopropoxy)carbonyl]benzene-1,4-dicarboxamide (PDPM) starting from pyromellitic dianhydride (PMDA) and *p*-phenylene diamine (*p*-PDA) as shown in Scheme 1. The new diamidodiamine, PDPM, is a diamine that contains an dianhydride moiety. PDPM was reacted with various dianhydrides to yield poly(amic acid-*alt*-amic esters) that can be thermally dehydrated to produce alternating copolyimides.^{6,7} Another method to prepare alternating copolyimides was reported by Mckerrow *et al.*⁸ The new diimidodiamine, *N,N*-bis(4-anilino)-1,2,4,5-benzene bis(dicarboximide) (4-ABI), was prepared from the corresponding dinitrocompound, which reacted with various dianhydrides to yield poly(amic acid-*alt*-imides), precursors for alternating copolyimides. (Scheme 1) However, 4-ABI has very low solubility so that the excess solvent has to be evaporated before casting films. On the contrary, the solubility of PDPM is high enough to produce a viscous solution of poly(amic acid-*alt*-amic esters) that is suitable to prepare high-quality polyimide films. The synthetic methodology employed to prepare PDPM has been applied to prepare various diamidodiamines from the commercial aromatic dianhydrides and diamines.⁷

To complement the previous study, we were interested in the preparation of diamidodianhydride, which contains diamine moiety as depicted in Scheme 2. From this new diamidodianhydride and a diamine, it is possible to prepare an alternating copolyimide with two different diamine moieties alternating after a dianhydride (Scheme 2). Whereas the reaction of a diamidodiamine such as PDPM with a dianhydride produces another alternating copolyimide with two different dianhydride moieties alternating after a diamine moiety (Scheme 1).

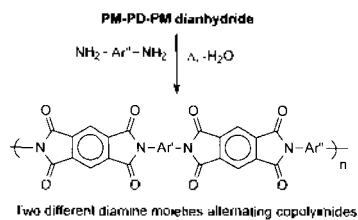
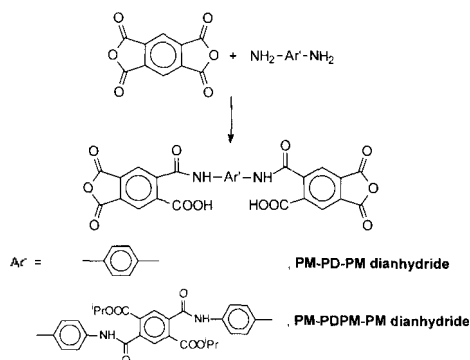
The diamidodianhydride shown in Scheme 2 may be produced simply by the addition of 2 equiv. of dianhydride to



Scheme 1

1 equiv. of diamine. But this usually ended up producing mixtures, including oligomers. Hodgkin has reported that complicated reaction mixtures were obtained due to the formation of oligomers in the attempt to prepare 4-ABI by mixing one equiv. of PMDA with two equiv. of *p*-PDA.⁹ The synthesis of 4,4-bis(5-carboxy-1,3-dioxo-2-oxaindan-6-carboxamido)benzene, which was denoted as PM-PD-PM dianhydride in Scheme 2, could be accomplished by slow addition of 1 equiv. of *p*-PDA (0.1 mole) to the tetrahydrofuran (THF) solution of 4 equiv. of PMDA at 0 °C. In practice, after one drop of *p*-PDA solution was added and yellow precipitate was formed, which usually took approximately one minute, the rest of the *p*-PDA solution was added dropwise to the stirring solution of PMDA at 0 °C. Since the PM-PD-PM dianhydride precipitated out from the THF solution as it was formed, no oligomer was formed. To minimize contact with moisture during isolation, the reaction mixtures were transferred into centrifugal tubes and the following sequence was repeated three times: centrifuging, decanting the supernatant, addition of fresh dry THF and mixing by shaking. Finally, the supernatant THF was decanted and the product (92% yield based on *p*-PDA; above 95% purity) was isolated after drying in a vacuum oven at 50 °C for one day.

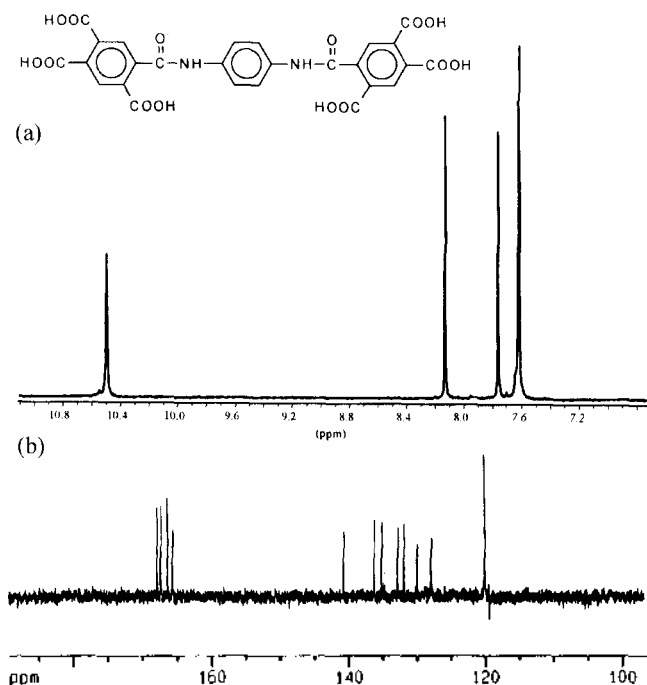
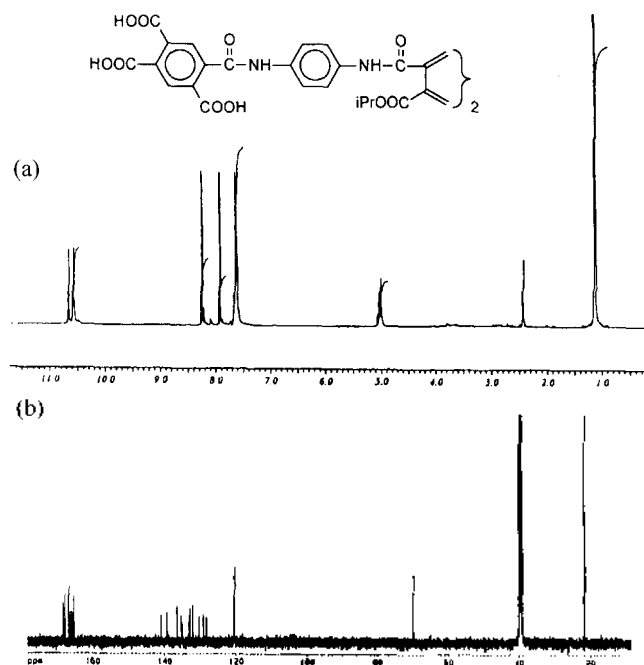
NMR characterizations were conducted with the corre-



Scheme 2

spending acid form of the dianhydride since the dianhydride rapidly reacted in solution with the residual water in DMSO-d₆. Figure 1 shows ¹H and ¹³C NMR spectra of the corresponding PM-PD-PM acid.¹⁰

Similarly, when PDPM was used instead of p-PDA, a new dianhydride, PM-PDPM-PM dianhydride, was prepared which contained four imide precursor moieties. (Scheme 2). In this case, due to the low solubility of PDPM in THF, 0.522 g of PDPM was dissolved in 5 mL of DMF and diluted with 45 mL of THF. After following the same sequences, PM-PDPM-PM dianhydride was

Figure 1. a) ¹H- and b) ¹³C NMR spectra of PM-PD-PM acid.Figure 2. a) ¹H- and b) ¹³C NMR spectra of PM-PDPM-PM acid.

obtained in 90% yield. This dianhydride was also converted into the corresponding acid for NMR characterization. (Figure 2)¹¹

These new dianhydrides prepared in this study are useful monomers for the syntheses of well-defined structures of copolyimides, copolyamide-imides, and polyimide-silica hybrids, which are currently under review.

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References

1. Sroog, C. E. *J. Polym. Sci., Macromol. Rev.* **1976**, *11*, 161.
2. Satou, H.; Suzuki, H.; Makino, D. In *Polyimides*; Wilson, D., Stenzenberger, H. D., Hergenrother, P. M., Eds.; Blackie: Glasgow, UK, 1990; p 227.
3. Ferger, C.; Franke, H. In *Polyimides Fundamentals and Applications*; Ghosh, M. K., Mittal, K. L., Eds.; Marcel Dekker, Inc.: New York, U.S.A., 1996; p 759.
4. Arnold, F. E. Jr.; Cheng, S. A. D.; Hsu, S. L. C.; Lee, C. J.; Harris, F. W.; Lau, S. F. *Polymer* **1992**, *33*, 5179.
5. Rhee, S. B.; Park, J. W.; Moon, B. S.; Chang, J. Y. *Macromolecules* **1993**, *26*, 404.
6. Park, J. W.; Lee, M.; Lee, M.-H.; Liu, J. W.; Kim, S. D.; Chang, J. Y.; Rhee, S. B. *Macromolecules* **1994**, *27*, 3459.
7. Rhee, S. B.; Park, J. W.; Moon, B. S.; Lee, M.-H.; Chang, J. Y. *Macromol. Chem. Phys.* **1995**, *196*, 691.
8. Mckerrow, A. J.; Fox, M. A.; Leu, J.; Ho, P. S. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 319.
9. Hodgkin, J.; Hawthorne, G.; Jackson, M.; Morton, T. *Polym. Prepr.* **1994**, *35(2)*, 375.
10. The spectral properties of the PM-PD-PM acid are as follows: ¹H NMR (δ, ppm, DMSO): 7.6 (s, 4H), 7.8 (s,

2H), 8.1 (s, 2H), 10.5 (s, 2H); ^{13}C NMR (δ , ppm, DMSO): 120.0, 127.8, 129.8, 131.7, 132.6, 135.0, 136.1, 140.6, 165.5, 166.2, 167.1, 167.8.

11. The spectral properties of the PM-PDPM-PM acid are as follows: ^1H NMR (δ , ppm, DMSO): 1.1 (s, 12H), 5.0 (s,

2H), 7.6 (s, 8H), 7.9 (s, 2H), 8.2 (s, 4H), 10.6 (s, 2H), 10.7 (s, 2H); ^{13}C NMR (δ , ppm, DMSO): 21.6, 69.9, 120.3, 120.4, 128.1, 129.0, 130.2, 132.0, 132.7, 133.1, 134.9, 135.3, 136.4, 139.2, 140.8, 165.1, 165.6, 166.0, 166.5, 167.5, 168.1.
