A New Class of Aromatic Dianhydrides for Thermostable Polyimides

Christopher J. Walsh and Braja K. Mandal*

Chemistry Division, Department of Biological,
Chemical and Physical Sciences, 3101 South
Dearborn Street, Illinois Institute of Technology,
Chicago, Illinois 60616

Received February 1, 2001
Revised Manuscript Received June 29, 2001

Aromatic polyimides, by virtue of their outstanding thermal, mechanical, and electrical properties, have secured a permanent place in a variety of industrial applications ranging from dielectric films for the electronic industry, to lightweight load-bearing heat-resistant composites and adhesives for the aerospace industry, to gas-separation membranes.[1] Recently, polyimides have been attracting considerable technical interest, particularly in the design of photorefractive and second-order nonlinear optical (NLO) polymers to improve the temporal stability of poled polymer films[2] and in the development of novel photoresists to simplify semiconductor fabrication as well as to distribute on-chip optical signals via waveguiding.[3] Therefore, the development of polyimides with novel combinations of properties continues to be an important research area.

Polyimides have been prepared by several routes. The widely used method for making polyimides is by reacting a dianhydride with a diamine.[1] Other approaches involve a nitro-displacement reaction[4] of a dinitro bisimide and a diphenoxide and the palladium-catalyzed carbonylation of a bis(*o*-iodo ester) and a diamine.[5] In general, aromatic polyimides with linear backbones such as the one derived from pyromellitic dianhydride (PMDA) and *p*-phenylene diamine are often difficult to process because of their insolubility in organic solvents. The two key factors in designing soluble and processable polyimides are (1) breaking the rigidity or regularity of the backbone and (2) minimizing the density of imide rings along the backbone. Progress has been made on these issues (i) by using enlarged dianhydrides such as 4,4′-(hexafluoroisopropylidene) diphthalic anhydride (6FDA), (ii) by incorporating hinges such as an oxygen atom into the diamine as in oxydianiline, and (iii) by placing aliphatic side chains in the diamine.[1,6] However, these hinges break the fully aromatic backbone of the polymer, resulting in a lower glass transition temperature (T_g) and decreased thermal stability. Therefore, the design and synthesis of purely aromatic monomers that will lead to processable polyimides is desirable. In the past, less emphasis has been placed on the structural modifications of polyimides that involve the synthesis of novel aromatic dianhydrides because of synthetic challenges.[7−12] In this work, we report a method for the preparation of functionalized dianhydrides that can be used in the synthesis of fully aromatic polyimides. In Figure 1, we show the structures of the three dianhydrides (**1**−**3**) prepared in this study. The synthesis of **3** represents a general approach to novel polyphenylated structures, which complements our earlier work on polyphenylated phthalocyanines, polyphenylated polyphenylenes, and carbazole-containing polyphenylated benzenes.[13−15]

The synthesis of **1** is shown in Scheme 1. Starting from commercially available 3-nitrophthalic acid, diethyl 3-iodophthalate, **4**, was prepared in yields of up to 80% by esterification, reduction, and diazotization.[16] Two equivalents of **4** were coupled with the benzene 1,4-diboronate ester,[17] using modified Suzuki conditions,[18] to produce tetraester **5**[19] in 79% yield. Hydrolysis of the tetraester using alcoholic potassium hydroxide followed

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* To whom correspondence should be addressed. E-mail: mandal@iit.edu.

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[19] Tetraethyl-2,2′,3,3′-*p*-terphenyltetracarboxylic Ester (**5**). To a 200-mL flask were added 5.00 g (14.39 mmol) of diethyl 3-iodophthalate, 2.5 g (7.67 mmol) of cesium carbonate, 1.0 g of 10% Pd/C, and a stir bar. The solids were dissolved in 50 mL of 95% ethanol, and 1.437 g (6.9 mmol, 0.48 equivalents) of the benzene-1,4-diboronate ester was added in one portion. A reflux condenser was attached to the flask, and the contents were heated at reflux overnight. After 12 h, an additional 1.5 g of cesium carbonate was added in portions, and the reaction mixture was stirred for 2 h. The solution was cooled to room temperature and filtered through a bed of Celite to remove the catalyst. The filtrate was cooled in an ice bath and brought to neutral pH. To the flask were added 20 mL of diethyl ether and 20 mL of water. The organic layer was separated and dried over sodium sulfate, and the solvent was removed to give the crude solid. The product was purified over silica gel using ethyl acetate/hexane as the eluent to give 2.84 g (79%), mp 107.5−108 °C. FTIR (neat): 3074, 2982, 1726, 1582, 1560, 1466, 1444, 1271, 1204, 1060, 1016, 857, 760, 699 cm^{-1}. MS (*m/z*): 518, 473, 427, 399, 371, 353, 325, 297, 226, 186. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.6−7.45 (m, 4H), 7.45−7.37 (m, 6H), 4.37 (q, 4H), 4.16 (q, 4H), 1.38 (t, 3H), 1.13 (t, 3H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 168.6, 165.8, 140.0, 139.0, 135.8, 134.0, 129.1, 128.6, 61.6, 61.4, 14.02, 13.83. Anal. Calcd for $C_{30}H_{30}O_8$: C, 69.49; H, 5.83. Found: C, 69.37; H, 5.80.

10.1021/cm010078u CCC: $20.00 © 2001 American Chemical Society
Published on Web 07/27/2001

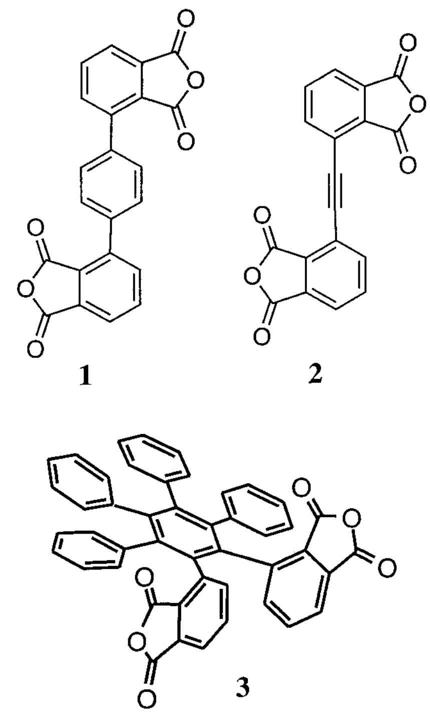
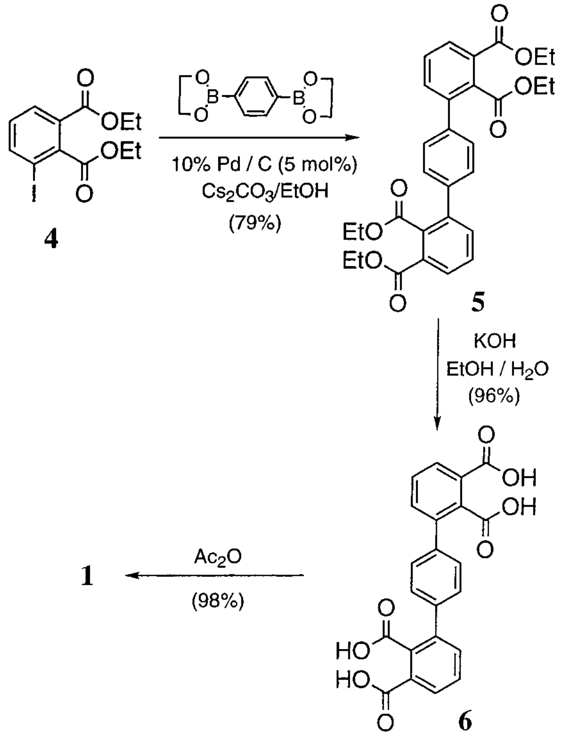


Figure 1. Structures of new dianhydrides.

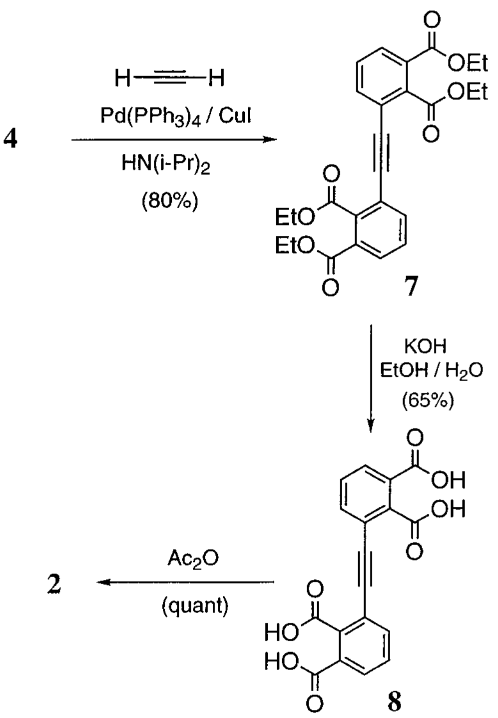
Scheme 1



by acidification gave the tetraacid **6**,[20] which underwent dehydration with acetic anhydride to give **1**[21] in quantitative yield.

The synthesis of **2** is depicted in Scheme 2. Cross-coupling between 2 equiv of **4** and acetylene, using Pd(PPh_3)$_4$ and CuI as catalysts, gave the acetylene-linked tetraester **7**[22] in 80% yield. Alkaline hydrolysis of **7** gave the tetraacid **8**,[23] which, upon dehydration, provided the dianhydride **2**[24] in good yield.

Scheme 2



The acetylene-linked tetraester **7** behaves as an excellent dienophile to produce a wide variety of polyaryl-substituted dianhydrides. Thus, **7** reacted in a sealed tube with tetracyclone at 215 °C to give polyphenylated tetraester **9**[25] in 60% yield (Scheme 3). Whereas hydrolysis of **9** proceeded normally, we found that some of the resulting tetraacid, **10**,[26] spontaneously dehydrated to yield a mixture of anhydrides and acids. Dehydration of the mixture with acetic anhydride gave **3**[27] in 95% yield.

The efficiency of this sequence of reactions to prepare the dianhydrides demonstrates the general utility of this method and establishes diethyl 3-iodophthalate, **4**, as an effective dianhydride synthon for zigzag polyimide synthesis.

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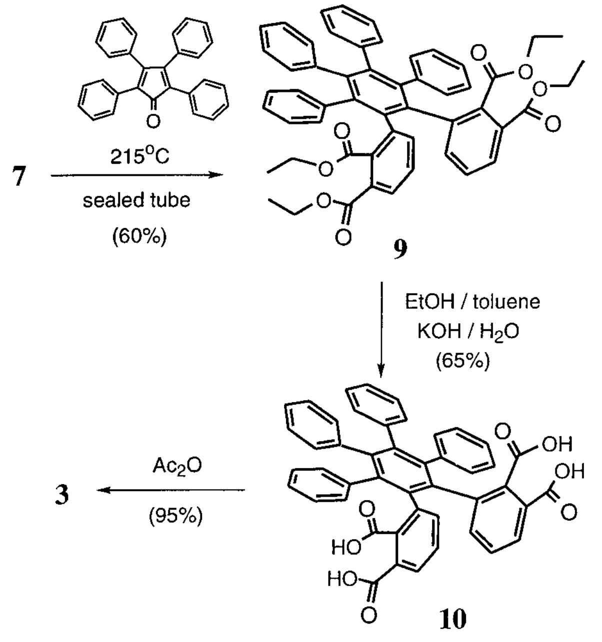
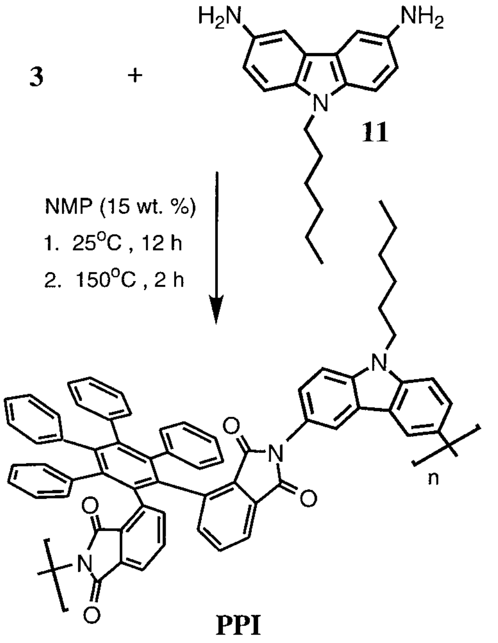
(20) 2,3′,3,3′-*p*-Terphenyltetracarboxylic Acid (**6**). In a 250-mL single-necked flask were placed 1.46 g (2.816 mmol) of **5** and 25 mL of ethanol. To the solution was added in portions 1.58 g of potassium hydroxide as an aqueous solution. The mixture was brought to reflux and heated with stirring for 1 h. FTIR analysis confirmed complete hydrolysis. The solvent was removed under reduced pressure, and the flask was connected to a vacuum pump and warmed for 15 min. The flask was allowed to cool to room temperature and was then warmed for 15 min. This process was repeated until the amorphous solid completely dried and solidified. The solid was dissolved in water, cooled in an ice bath, and acidified using concentrated hydrochloric acid. The precipitate was collected by suction filtration, washed with water, and dried in an oven. The product, **6**, was sufficiently pure to be used in the next step and totaled 1.1 g (96%), mp >350 °C. FTIR (neat): 2922, 2854, 2661, 1693, 1587, 1463, 1416, 1377, 1276, 1112, 929, 827, 774, 616 cm^{-1}. ^{1}H NMR (300 MHz, d$_6$-acetone): δ 13.14 (s, 4H), 7.63−7.55 (m, 4H), 7.50−7.46 (m, 6H). ^{13}C NMR (75 MHz, d$_6$-acetone): δ 170.20, 168.01, 139.64, 139.36, 136.13, 134.9, 134.53, 130.02, 129.61, 129.11. Anal. Calcd for $C_{22}H_{14}O_8$: C, 65.02; H, 3.47. Found: C, 64.87; H, 3.50.

(21) 2,2′,3,3′-*p*-Terphenyltetracarboxylic Dianhydride (**1**). To a 100-mL flask equipped with a reflux condenser was added 1.18 g of **6** and 25 mL of freshly distilled acetic anhydride. The mixture was brought to reflux temperature and stirred for 30 min. The solid never dissolved. The mixture was cooled to room temperature and filtered. The product was washed with dry diethyl ether and dried in an oven to give pure **1** as white needles, mp > 350 °C. FTIR (neat): 2924, 2854, 1846, 1780, 1463, 1377, 1261, 1206, 1132, 898, 846, 809, 790, 735, 680 cm^{-1}. Anal. Calcd for $C_{22}H_{10}O_6$: C, 71.35; H, 2.72. Found: C, 71.40; H, 2.80. This anhydride was previously prepared by Berlin et al. following a Diels−Alder reaction between 1,4-bis-(α-furyl)-benzene and maleic anhydride. See: Berlin, A. A.; Liogonky, B. I.; Zapadinsky, B. I. U.S. Patent 3,891,633, 1975.

Scheme 3



Scheme 4



In seeking to prepare a fully soluble and thermally resistant polyimide, we chose the polyphenylated dianhydride **3** as a representative example in a polymerization reaction with an aromatic diamine. The diamine selected in this study was 3,6-diamino-9-hexylcarbazole, **11**.[28] Materials containing carbazole moieties are attractive for xerographic,[29] photorefractive,[30] and light-emiitting[31] applications because of their superior charge-transport properties. We surmised that incorporating carbazole could lead to new highly stable materials with improved charge-transport properties.

As shown in Scheme 4, the polymerization of **3** with **11** was carried out using a two-step, polyamic acid precursor method. The monomers reacted at room temperature in NMP as a 10 wt % solution and then were heated to 150 °C for 2 h to complete imidization.[32] The reaction was followed by FT-IR spectroscopy by monitoring the loss of the anhydride and amine stretching bands. The representative polyimide **PPI** was completely soluble in chloroform, methylene chloride,

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(22) 1,2-Di-(diethyl 3-phthalate)ethyne (**7**). Into a 250-mL oven-dried flask were added 5.0 g (14.367 mmol) of **4**, 2 mol % of CuI, and 3 mol % of Pd(PPh_3)$_4$, followed by 50 mL of anhydrous diisopropylamine. The solution was stirred at room temperature, and acetylene gas was introduced below the surface of the solution and bubbled for 10 min. The acetylene was removed, and the reaction mixture was allowed to continue stirring for 30 min. Acetylene was reintroduced for 10 min and again removed, allowing the reaction to stir for 30 min. This process was continued until the reaction was deemed complete by TLC analysis. The reaction mixture was filtered, and the filtrate solvent was removed under reduced pressure. The solid was collected and chromatographed over neutral alumina using ethyl acetate/hexane to give **7** in pure form, 5.35 g (79%), mp 130−132 °C. FTIR (neat): 2986, 2906, 1740, 1719, 1587, 1475, 1453, 1365, 1323, 1266, 1201, 1158, 1116, 1064, 1034, 761 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.01 (d, 2H), 7.70 (d, 2H), 7.47 (t, 2H), 4.47 (q, 4H), 4.37 (q, 4H), 1.37 (q, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.8, 165.0, 138.2, 136.2, 130.3, 139.1, 128.5, 121.2, 89.7, 62.0, 61.8, 14.16. Anal. Calcd for $C_{26}H_{26}O_8$: C, 66.94; H, 5.62. Found: C, 67.06; H, 5.52.

(23) 1,2-Di-(3-phthalic acid)ethyne (**8**). This compound was made following the procedure described for compound **6** and was isolated in 65% yield, mp 328−330 °C. FTIR (neat): 2923, 2854, 1701, 1590, 1464, 1377, 1270, 1244, 1134, 1016, 832, 808, 766, 747, 665 cm^{-1}. Anal. Calcd for $C_{18}H_{10}O_8$: C, 61.03; H, 2.84. Found: C, 60.82; H, 3.02.

(24) 1,2-Di-(3-phthalic anhydride)ethyne (**2**). This compound was made following the procedure described for compound **1** and was obtained in nearly quantitative yield, mp >350 °C. FTIR (neat): 2933, 2854, 2319, 1844, 1789, 1664, 1459, 1376, 1169, 1082, 906, 737 cm^{-1}. Anal. Calcd for $C_{18}H_6O_6$: C, 67.94; H, 1.90. Found: C, 67.79; H, 1.78.

(25) 1,2-Di-(diethyl 3-phthalate)-3,4,5,6-tetraphenylbenzene (**9**). Into a 25-mL ampule were added 1.0 g of **7**, 1.10 equiv of tetracyclone, and five drops of cyclohexylbenzene. The ampule was degassed with several freeze−pump−thaw cycles and sealed under vacuum with a flame torch. The sealed tube was placed in an oven set at 215 °C for 24 h. The tube was allowed to cool and was then broken open (*Caution:* Contents may be under pressure!), and the solids were dissolved in dichloromethane and deposited onto silica gel. The crude mixture was chromatographed over silica using ethyl acetate/hexane as the eluent and pure **9** was isolated, 1.55 g (60%), mp 156−158 °C. FTIR (neat): 3056, 2982, 1725, 1591, 1496, 1444, 1272, 1188, 1144, 1026, 764, 700 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.79 (d, 2H), 7.38 (d, 2H), 7.05 (t, 2H), 6.94−6.67 (m, 20H), 4.28−4.04 (m, 8H), 1.28 (t, 6H), 1.22 (t, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.6, 167.0, 140.8, 140.3, 139.9, 139.8, 139.0, 137.5, 135.8, 133.7, 131.8, 131.2, 130.3, 128.2, 127.7, 126.6, 126.5, 125.8, 125.3, 61.3, 61.0, 14.1, 13.8. Anal. Calcd for $C_{54}H_{46}O_8$: C, 78.81; H, 5.63. Found: C, 78.85; H, 5.61.

(26) 1,2-Di-(3-phthalic acid)-3,4,5,6-tetraphenylbenzene (**10**). This compound was prepared in exactly the same manner as compound **6** in 65% yield, mp >350 °C. FTIR (neat): 1847, 1783, 1696, 1495, 1442, 1406, 1350, 1263, 1213, 1127, 896, 760, 699 cm^{-1}. No analysis was performed because of the mixture of anhydride and acid peaks in the FTIR spectrum.

(27) 1,2-Di-(3-phthalic anhydride)-3,4,5,6-tetraphenylbenzene (**3**). This compound was prepared in the same manner as compound **1** in 95% yield. FTIR (neat): 1846, 1787, 1495, 1408, 1352, 1264, 1128, 898, 700 cm^{-1}. Anal. Calcd for $C_{46}H_{26}O_6$: C, 81.89; H, 3.88. Found: C, 81.79; H, 3.74.

(28) See Supporting Information for a detailed synthesis of **11**.

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(32) **PPI**. Into a flame-dried flask were placed both the dianhydride **3** and the diamine **11** with a stir bar. Anhydrous *N*-methyl pyrrolidone was added so that the total weight percent of the monomers was 10−15%. The reaction mixture was stirred at room temperature for 12 h and heated to 150 °C for 2 h to complete the imidization of the precursor polyamic acid. The resulting solution was cooled to room temperature and poured into methanol to precipitate the polyimide. The solids were collected by filtration, washed with methanol, and extracted with methanol overnight in a Soxhelet extractor. The solid (white powder) was dried in a drying pistol over phosphorus pentoxide at 120 °C. Yield: 64%. FTIR (neat): 3056, 2929, 1775, 1719, 1493, 1375, 1306, 1237, 1105, 1023, 753, 699. Anal. Calcd for $C_{64}H_{45}N_3O_4$: C, 83.55; H, 4.93; N, 4.57. Found: C, 82.81; H, 4.76; N, 4.51. ^1H NMR (300 MHz, $CDCl_3$): δ 8.32−6.81 (m), 4.30 (t), 1.44−1.20 (m), 0.87 (t).

and THF. We attribute the improved solubility to the orthogonal phenyl rings in the molecular structure.[13] The inherent viscosity of **PPI** was measured at 0.38 dL gg^{-1} using a *N*,*N*-dimethylacetamide (DMAc) solution at a concentration of 0.5 g dL^{-1} at 30 °C. Thermal analysis was performed on the material and showed only a 5% weight loss at 500 °C.[33] A 10% weight loss occurred at 555 °C, which is impressive for a material that is fully soluble and contains some aliphatic segments. No glass transition temperature, T_g, could be established under 320 °C, indicating the presence of a very rigid backbone.

Thus, we have demonstrated that a new class of dianhydrides can be prepared by cross-coupling between diethyl-3-iodophthalate and benzene-1,4-diboronate ester or acetylene. The acetylenic tetraester is an efficient dienophile in 4 + 2 cycloaddition with tetracyclone to give the polyphenylated tetraester. The polyphenylated dianhydride, when polymerized with a carbazole-based diamine, gave a novel soluble polyimide that exhibits excellent thermal properties. Experiments involving charge-transport properties of this polymer are in progress, and these results, along with reports of other aryl- and heteroaryl-substituted polyimides, will be presented in the future.

Supporting Information Available: Detailed syntheses of **4** and **11** and TGA trace of **PPI**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(33) See Supporting Information for the TGA trace.