Macromolecules **1999,** *32,* 3598−3612

Thermal Conversion of Hydroxy-Containing Imides to Benzoxazoles: Polymer and Model Compound Study

Gordon L. Tullos, Jason M. Powers, Stacy J. Jeskey, and Lon J. Mathias*

The University of Southern Mississippi, Southern Station Box 10076, Hattiesburg, Mississippi 39406

Received October 8, 1998; Revised Manuscript Received March 29, 1999

ABSTRACT: A series of hydroxy-containing polyimides, containing pendent hydroxyl groups ortho to the heterocyclic imide nitrogen, were prepared via the solution condensation of aromatic dianhydrides with bisaminophenols. The polyimides were found to undergo thermal conversion to polybenzoxazoles upon heating between 350 and 500 °C under nitrogen or vacuum. The thermal conversion was accompanied by loss of carbon dioxide. No other volatile byproducts were detected by IR or NMR. Structures were confirmed by IR, solid-state NMR, and elemental analysis. Polybenzoxazole films, obtained by the thermolysis of solvent-cast poly(amic acid) or polyimide solutions, displayed excellent solvent resistance and good thermal stability. Insolubility of the polybenzoxazoles in all solvents tested indicates possible cross-linking. No crystallinity was observed by X-ray diffraction. Due to the insolubility of the resulting polybenzoxazoles, model compound reactions were also investigated. In the vapor phase at 400 °C, *N*-(2-hydroxyphenyl)phthalimide underwent intramolecular thermal conversion to 2-phenylbenzoxazole in 83% yield, emulating the polyimide reactions. Thermal conversion of *N*-(2-hydroxyphenyl)phthalimide in the melt at 400 °C resulted in the formation of intermolecular reaction products. The intermolecular reactions may be a source of possible cross-links, which would explain the insolubility of the polybenzoxazoles.

Introduction

Reaction of aromatic dianhydrides with aromatic bis(*o*-diamines) leads to the formation of thermally stable semiladder or ladder polyimidazopyrrolones (pyrrones). These polymers have been formed under melt and solution reaction conditions. It is known that the reaction of dianhydrides with bis(*o*-diamines) results in the initial formation of soluble imide−amine and carboxy−imidazole polymer precursor intermediates which subsequently cyclize, with loss of water, to the final polyimidazopyrrolones at elevated temperature. The polymer-forming reactions have been studied in some detail in the melt and in solution utilizing phthalic anhydride and *o*-phenylenediamine as model compounds. Reaction of phthalic anhydride with *o*-phenylenediamine in the melt and in solution at moderate temperatures results in the formation of *N*-(2-aminophenyl)phthalimide and 2-(2-carboxyphenyl)benzoxazole. Both compounds undergo thermal conversion with loss of water at elevated temperature to give the same tetracyclic pyrrone (1,2-benzoylenebenzimidazole).[1−4]

Soluble hydroxy-containing polyimides have recently been studied as potential high glass transition temperature (T_g), thermally stable polymers for photoresist[5−7] and nonlinear optical (NLO) applications.[8] The hydroxy-containing polyimides are prepared by the reaction of aromatic dianhydrides with aromatic bis(*o*-aminophenols) in polar aprotic solvents, a reaction similar to the formation of polyimidazopyrrolone precursors. We became interested in potential use of hydroxy-containing polyimides for incorporation of other useful functionality. The pendent hydroxyl group on the fully imidized polymer is available for postpolymerization reactions (such as NLO chromophore attachment) under mild reaction conditions.[9] During the process of characterizing these materials, we discovered an unexpected thermogravimetric analysis (TGA) weight loss (corresponding to one CO_2 per imide) that implied in-situ thermal conversion of the hydroxy-containing polyimides to aromatic polybenzoxazoles.[10] The thermal conversion of hydroxy-containing polyimides to polybenzoxazoles appears to be similar in many respects to the thermal formation of tetracylic polyimidazopyrrolones. However, the hydroxy-containing polyimides lack the functionality necessary to form stable tetracyclic ring structures upon thermal conversion, and thus polybenzoxazoles are the result.

Aromatic polybenzoxazoles (PBOs) display excellent thermal stability plus good solvent and chemical resistance.[11] The properties of aromatic polybenzoxazoles that make them attractive for many applications also lead to difficulties in synthesis and fabrication. Wholly aromatic PBOs, in fact, are soluble only in strong acids (e.g., sulfuric, methanesulfonic, triflic, and polyphosphoric acids)[12,13] and more recently through complex-mediated solublization in Lewis acid/solvent systems such as $AlCl_3$/nitromethane.[14] In-situ thermal conversion of hydroxy-containing polyimides to PBOs could provide an alternative method for generating PBO films, fibers, and composites that are difficult or impossible to obtain otherwise. In fact, thermal rearrangement of precursor polymers to PBO's has been described based on aramids. Intramolecular nucleophilc aromatic substitution involving displacement of a cyano group, for example, by the amide oxygent resulted in formation of the benzoxazole ring.[15] This paper describes our results concerning the thermal conversion of hydroxy-containing polyimides to polybenzoazoles and model compounds to benzoxazoles.

Experimental Section

3,3′-Dihydroxy-4,4′-diaminobiphenyl (HAB) from Chriskev Co., Inc., was purified by forming a saturated solution in DMAc at 100 °C then filtering through a Celite pad followed by addition of the filtrate to twice the volume of stirred ethanol. The light-tan HAB crystals that formed were collected by filtration, washed with ethanol, and dried under vacuum for 12 h at 120 °C. 3,3′,4,4′-Benzophenonetetracarboxylic dianhydride (BTDA) from Aldrich Chemical Co., Inc., was sublimed twice (250 °C, <1 mmHg) prior to use. 4,4′-Oxydiphthalic anhydride (ODPA) and 2,2-bis(3-amino-4-hydroxyphenyl)-hexafluoropropane (APAF) from Chriskev and 4,4′-(hexaflu-

10.1021/ma981579c CCC: $18.00

oroisopropylidene)diphthalic anhydride (6FDA) from Hoechst Celanese Corp. were sublimed at 250 °C at <1 mmHg prior to use. 3,3′,4,4′-Biphenyltetracarboxylic dianhydride (BPDA) from Chriskev and bisphenol A dianhydride (BPADA) from General Electric Co. were used as received. *N*-Methyl-2-pyrrolidinone (NMP) and *N*,*N*-dimethylacetamide were stirred over CaH_2 overnight and then distilled under reduced pressure and stored over 4 Å molecular sieves under nitrogen. Tetrahydrofuran (THF) was distilled from sodium/benzophenone. All other reagents and solvents were obtained commercially and used as received.

Solution ^1H and ^{13}C NMR were obtained on a Bruker AC-300 instrument using standard acquisition parameters. Solid-state ^{13}C NMR spectra were aquired on a Bruker MSL-400 spectrometer operating at a frequency of 100.61 MHz using cross-polarization/magic angle spinning (CP/MAS) and high-power proton decoupling with sample spinning rates >4.0 kHz. Fourier-transform infrared (FTIR) spectra were obtained on gas-phase samples via direct transfer line from the thermal gravimetric analysis (TGA) unit, solution-cast polymer thin films, and KBr pellet samples using an ATI-Mattson Galaxy 5020 spectrometer. Molecular weight data were obtained by size-exclusion chromatography (SEC) in tetrahydrofuran (THF) relative to polystyrene standards using four AM gel mixed bed 7.5 mm i.d. × 300 mm, 10 mm particle diameter columns (American Polymer Standards Corp., Mentor, OH). Differential scanning calorimetry (DSC) and TGA scans were conducted on TA Instruments 2920 and 2960 modules running at temperature ramp rates of 10 and 20 °C, respectively, both controlled by a Thermal Analyst 2100 data station. Melting points were obtained on a Mel-Temp hot-block melting point apparatus. Intrinsic viscosities were measured in *N*,*N*-dimethylacetamide (DMAc) using a Cannon-Ubbelohde #75 viscometer at 30 °C. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.

2,6-Dinitro-4-phenylphenol (DNPP). 4-Phenylphenol (20.00 g, 117.5 mmol) was dissolved in glacial acetic acid (100 mL) in a 250 mL Erlenmeyer flask. The stirred solution was cooled to 0 °C, and then 15 M HNO_3 (16 mL) was added dropwise over 10 min. The resulting yellow mixture was allowed to warm to room temperature and stirred for 2 h. The reaction mixture was diluted with water (100 mL). The yellow solid that formed was collected by filtration, washed with water, and dried. It was then dissolved in refluxing acetone (400 mL), and the hot solution was quickly filtered under aspiration through a medium glass frit to give a clear, orange filtrate which on cooling gave yellow-orange crystals of **DNPP**. The product was filtered and dried at 80 °C for 4 h in vacuo. Yield 26.01 g (85%); mp 155−157 °C. ^1H NMR (DMSO-d_6 with TMS): δ 11.03 (s, 1H), 8.42 (s, 2H), 7.70 (d, 2H), 7.41 (m, 3H). ^{13}C NMR (DMSO-d_6 with TMS) δ: 144.9, 140.5, 135.9, 130.9, 129.2, 128.5, 127.1, 126.5. Anal. Calcd for $C_{12}H_8N_2O_5$: C, 55.39; H, 3.10; N, 10.77%. Found: C, 55.48; H, 2.99; N, 11.01%.

2,6-Diamino-4-phenylphenol (DAPP). 2,6-Dinitro-4-phenylphenol (10.00 g, 38.4 mmol) was stirred in acetone (100 mL) in a 500 mL Erlenmeyer flask at 0 °C. Sodium hydrosulfite (53.53 g, 307 mmol) was mixed with water (160 mL) to form a white slurry. This slurry was added slowly to the flask over 10 min during which time the contents changed from orange to light-brown. The reaction mixture was allowed to warm to room temperature over 30 min with stirring. The mixture was diluted with water (100 mL), and the solids were collected by filtration. The resulting gray solid was washed with water and sublimed (200 °C, <1 mmHg) to give white crystals of **DAPP**. Yield 3.97 g (51%); mp 200−204 °C decomposition. ^1H NMR (DMSO-d_6 with TMS): δ 7.47 (s), 7.33 (s), 7.21 (s), 6.35 (s), 5.06 (s). ^{13}C NMR (DMSO-d_6 with TMS): δ 141.7, 137.9, 132.7, 130.2, 128.7, 126.1, 103.4. Due to the rapid oxidation of this material, elemental analysis was not attempted.

2,2-Bis(3-nitro-4-hydroxyphenyl)propane. Bisphenol A (20.0 g, 87.6 mmol) was dissolved in acetone (100 mL) in a 250 mL Erlenmeyer flask. The contents of the flask were stirred and cooled to 0 °C in an ice/water bath. Concentrated nitric acid (17 mL) was added dropwise form a separatory funnel over 30 min. The resulting thick, rusty-orange reaction mixture was allowed to stir for 12 h while warming to room temperature. Distilled water (50 mL) was then added slowly to the stirred reaction mixture over 10 min. The orange solid was collected by filtration and recrystallized from ethanol. The resulting yellow-orange needle crystals of 2,2-bis(3-nitro-4-hydroxyphenyl)propane were dried under vacuum for 6 h at 90 °C. Yield 16.1 g (58%); mp 133 °C (lit.[16] mp 133 °C). ^1H NMR ($CDCl_3$ with TMS): δ 10.52 (s, 2H, OH), 8.05−8.06 (d, 2H), 7.34−7.38 (q, 2H), 7.06−7.09 (d, 2H), 1.72 (s, 6H). ^{13}C NMR ($CDCl_3$ with TMS): δ 153.6, 141.7, 136.9, 133.0, 121.8, 120.2, 42.0, 30.3.

2,2-Bis(3-amino-4-hydroxyphenyl)propane (APA). 2,2-Bis(3-nitro-4-hydroxyphenyl)propane (10.0 g, 31.4 mmol) was placed in a 250 mL three-neck, round-bottom flask with 50 mL of ethanol and 10% Pd/C catalyst (0.5 wt %). The flask was fitted with a reflux condenser, dropping funnel, and nitrogen purge. Hydrazine hydrate ($H_2N{-}NH_2{\cdot}1.5H_2O$) (10 mL) was added to the stirred reaction mixture over 30 min. An exotherm was observed, and the reaction became deep-orange in color upon addition of the hydrazine hydrate. After addition was complete, the reaction was refluxed for 2 h, at which time the orange color had faded and a white precipitate formed. DMAc was added slowly to the refluxing mixture until the white precipitate dissolved. This solution was filtered hot under aspiration through filter paper to remove the Pd/C catalyst and give an orange filtrate. Upon recrystallizing overnight, APA was collected as tan needle crystals. Yield 4.1 g (51%); mp 269−272 °C decomposition (lit.[16] 271 °C decomposition). ^1H NMR (DMSO-d_6 with TMS): δ 8.75 (s, ~2H, OH), 6.55−6.58 (d, 2H), 6.46 (d, 2H), 6.33−6.36 (d, 2H), 4.36 (s, ~4H, NH_2), 1.49 (s, 6H). ^{13}C NMR (DMSO-d_6 with TMS): δ 142.4, 141.9, 135.6, 114.4, 113.7, 41.1, 31.2. Anal. Calcd for $C_{15}H_{18}N_2O_2$: C, 69.74; H, 7.02; N, 10.84%. Found: C, 70.00; H, 7.06; N, 10.82%.

Polyimide Synthesis (BPADA−DAPP). Polyimides were prepared by a conventional two-step process involving formation of the poly(amic acids) followed by thermal dehydration to the polyimides in solution. Polyimides which became insoluble upon solution dehydration were manipulated as poly(amic acid) solutions to form films. For example, to a 100 mL flask purged with nitrogen was added DAPP (2.000 g, 9.990 mmol) and NMP (15 mL). The mixture was stirred to form a clear, brown solution at ambient temperature. To this solution of diamine was added BPADA (5.200 g, 9.990 mmol) and NMP (20 mL) in order to achieve 20% (w/v) solids content. The reaction was mechanically stirred for 4 h at ambient temperature to give a viscous yellow poly(amic acid) solution. Toluene (25 mL) was added to the flask, and the poly(amic acid) was thermally cyclized in solution to the hydroxy-containing polyimide by refluxing for 3 h. Water was removed as the toluene/water azeotrope using a Dean-Stark trap. Excess toluene was then distilled from the solution followed by dilution of the cooled polymer solution with DMAc (100 mL). The solution was filtered to remove a small amount of gelatinous material and the filtrate precipitated into methanol to give a white solid which was dried in vacuo at 150 °C for 24 h. Yield 5.9 g (86%); $[\eta] = 1.63$ dL/g in DMAc; $T_g = 258$ °C by DSC; 5 wt % loss at 444 °C in air and 438 °C in N_2; char yield = 43% at 1000 °C in N_2; SEC (THF) $M_n = 180\,200$, $M_w = 316\,400$. IR (film): 3220 (O−H), 3058, 2968, 1779 (C=O), 1725 (C=O), 1600, 1504, 1479, 1358, 1275, 1239, 1100, 850 cm^{-1}. ^1H NMR ($CDCl_3$ with TMS): δ 7.85−7.88 (d, 2H), 7.59 (s, 2H), 7.53−7.56 (d, 2H), 7.30−7.41 (m, 11H), 7.00−7.03 (d, 4H), 6.83 (s, 1H, OH), 1.74 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$ with TMS): δ 166.9, 166.8, 164.0, 152.6, 147.6, 146.4, 139.0, 135.0, 134.4, 128.8, 127.6, 127.0, 126.1, 125.1, 123.3, 123.1, 120.1, 112.1, 42.6, 31.0. Anal. Calcd for $C_{43}H_{28}N_2O_7$: C, 75.43; H, 4.12; N, 4.09%. Found: C, 75.74; H, 4.32; N, 3.85%.

BPDA−HAB gave insoluble polyimide; $[\eta]$ [poly(amic acid)] = 0.82 dL/g in DMAc; cast films of the polyamic acid were dried under vacuum at 60 °C for 1 h and 120 °C for 2 h and then thermally cyclized to the hydroxy-containing polyimide at 300 °C for 1 h under nitrogen to give an insoluble material. No T_g was observed by DSC up to 500 °C; TGA 5 wt % loss in N_2 occurred at 422 °C with 18.6 wt % loss from 325 to 600 °C in nitrogen. Polyimide ^{13}C (CP/MAS): δ 167.5, 152.6, 142.6, 132.0, 118.9. IR (film): 3385 (O−H), 1775 (C=O), 1714 (C=O), 1380 cm^{-1}. Anal. Calcd for $C_{28}H_{14}N_2O_6$: C, 70.89; H, 2.97; N, 5.90%. Found: C, 70.64; H, 3.18; N, 5.94%.

BPDA−APAF gave insoluble polyimide; T_g = 354 °C by DSC; TGA 5 wt % loss at 349 °C in air and 387 °C in N_2; char yield = 52% at 1000 °C in N_2. Anal. Calcd for $C_{31}H_{14}F_6N_2O_6$: C, 59.63; H, 2.26; N, 4.49%. Found: C, 59.49; H, 2.21; N, 4.60%.

BPDA−APA gave insoluble polyimide; T_g = 344 °C by DSC; TGA 5 wt % loss at 353 °C in air and 350 °C in N_2; char yield = 35% at 1000 °C in N_2. Anal. Calcd for $C_{31}H_{20}N_2O_6$: C, 72.09; H, 3.90; N, 5.42%. Found: C, 70.35; H, 5.12; N, 5.99%.

BTDA−DAPP gave soluble polyimide; yield 2.8 g (78%); [η] = 0.50 dL/g in DMAc; T_g = 341 °C by DSC; 5 wt % loss at 455 °C in air and 446 °C in N_2; char yield = 54% at 1000 °C in N_2. IR (film): 3346 (O−H), 3065, 1781 (C=O), 1727 (C=O), 1674, 1487, 1425, 1359, 1247, 1101, 720 cm^{-1}. ^{1}H NMR (DMSO-d_6 with TMS) δ: 10.41 (s, 1H, OH), 8.25−8.30 (d, 6H), 7.94 (s, 2H), 7.63−7.65 (d, 2H), 7.48 (s, 2H), 7.35 (s, 1H). ^{13}C NMR (DMSO-d_6 with TMS): δ 193.4, 166.3, 150.8, 141.7, 138.0, 135.9, 135.1, 132.3, 131.1, 129.5, 129.1, 127.4, 125.9, 124.0, 120.7. Anal. Calcd for $C_{29}H_{14}N_2O_6$: C, 71.61; H, 2.90; N, 5.76%. Found: C, 71.36; H, 3.07; N, 5.55%.

6FDA−DAPP gave soluble polyimide; yield 4.9 g (80%); [η] = 0.30 dL/g in DMAc; T_g = 329 °C by DSC; 5 wt % loss at 463 °C in air and 456 °C in N_2; char yield = 51% at 1000 °C in N_2; SEC (THF) M_n = 3800, M_w = 10 400. IR (film): 3247 (O−H), 3068, 2931, 1787 (C=O), 1729 (C=O), 1426, 1358, 1255 (C−F stretch), 1210, 1193, 1105, 722 cm^{-1}. ^{1}H NMR (DMSO-d_6 with TMS) δ: 10.28 (s, 1H, OH), 8.25−8.27 (d, 2H), 8.03 (s, 2H), 7.93 (s, 2H), 7.82 (s, 2H), 7.59−7.61 (d, 2H), 7.44−7.49 (t, 2H), 7.34−7.36 (d, 1H). ^{13}C NMR (DMSO-d_6 with TMS): δ 166.2, 166.0, 150.9, 137.9, 137.4, 135.9, 133.4, 133.0, 131.1, 129.5, 129.1, 127.4, 125.8, 125.3, 124.5, 123.7, 121.5, 120.5, 117.7. Anal. Calcd for $C_{31}H_{14}F_6N_2O_5$: C, 61.19; H, 2.32; N, 4.60%. Found: C, 60.96; H, 2.22; N, 4.55%.

ODPA−APAF gave soluble polyimide; yield 9.16 g (88%); [η] = 0.42 dL/g in DMAc; T_g = 295 °C by DSC; 5 wt % loss at 397 °C in air and 400 °C in N_2; char yield = 45% at 1000 °C in N_2; SEC (THF) M_n = 4300, M_w = 15 300. IR (film): 3401 (O−H), 3074, 1784 (C=O), 1718 (C=O), 1612, 1520, 1477, 1441, 1381, 1260 (C−F stretch), 1109 cm^{-1}. ^{1}H NMR (DMSO-d_6 with TMS): δ 10.51 (s, 2H, OH), 8.01−8.04 (d, 2H), 7.62 (s, 4H), 7.42 (s, 2H), 7.23−7.25 (d, 2H), 7.08−7.11 (d, 2H). ^{13}C NMR (DMSO-d_6 with TMS): δ 166.2, 166.0, 160.8, 154.9, 134.9, 132.0, 131.7, 127.6, 126.0, 124.8, 122.3, 118.7, 116.8, 113.8. Anal. Calcd for $C_{31}H_{14}N_2O_6F_6$: C, 58.14; H, 2.20; N, 4.37%. Found: C, 56.17; H, 2.76; N, 4.16%.

ODPA−APA gave soluble polyimide; yield 4.19 g (98%); [η] = 0.53 dL/g in DMAc; T_g = 278 °C by DSC; 5 wt % loss at 391 °C in air and 404 °C in N_2; char yield = 25% at 1000 °C in N_2. IR (film): 3401 (O−H), 2970, 1778 (C=O), 1716, 1610, 1512, 1431, 1387, 1273, 1232, 1107, 839, 773 cm^{-1}. ^{1}H NMR (DMSO-d_6 with TMS): δ 9.73 (s, 2H, OH), 8.02−8.04 (d, 2H), 7.63 (s, 4H), 7.24 (s, 2H), 7.12−7.14 (d, 2H), 6.91−6.93 (d, 2H), 1.61 (s, 6H, CH_3). ^{13}C NMR (DMSO-d_6 with TMS): δ 166.5, 166.3, 160.8, 151.7, 141.2, 134.8, 128.9, 127.7, 127.6, 125.9, 124.8, 118.1, 116.2, 113.7, 41.2, 30.8. Anal. Calcd for $C_{31}H_{20}N_2O_6$: C, 69.92; H, 3.79; N, 5.26%. Found: C, 69.70; H, 4.04; N, 5.26%.

BPADA−APAF gave soluble polyimide; yield 4.31 g (74%); [η] = 0.44 dL/g in DMAc; T_g = 251 °C by DSC; 5 wt % loss at 399 °C in air and 395 °C in N_2; char yield = 48% at 1000 °C in N_2; SEC (THF) M_n = 40 500, M_w = 74 000. IR (film): 3346 (O−H), 2972, 1780 (C=O), 1724 (C=O), 1618, 1518, 1479, 1383, 1236 (C−F stretch), 1173, 1107, 850 cm^{-1}. ^{1}H NMR (DMSO-d_6 with TMS): δ 10.50 (s, 2H, OH), 7.90−7.93 (d, 2H), 7.34−7.38 (t, 10H), 7.21−7.24 (d, 2H), 7.07−7.14 (t, 6H), 1.70 (s, 6H, CH_3). ^{13}C NMR (DMSO-d_6 with TMS): δ 166.3, 166.2, 162.6, 154.8, 152.7, 147.0, 134.7, 132.0, 131.7, 128.6, 125.9, 125.8, 122.8, 122.2, 119.7, 118.8, 116.8, 111.6, 42.1, 30.6. Anal. Calcd for $C_{46}H_{26}F_6N_2O_8$: C, 64.95; H, 3.32; N, 3.29%. Found: C, 65.09; H, 3.46; N, 3.26%.

BPADA−APA gave soluble polyimide; yield 4.94 g (73%); [η] = 0.86 dL/g in DMAc; T_g = 238 °C by DSC; 5 wt % loss at 380 °C in air and 405 °C in N_2; char yield = 25% at 1000 °C in N_2; SEC (THF) M_n = 45 100, M_w = 100 800. IR (film): 3384 (O−H), 2970, 2875, 1778 (C=O), 1714 (C=O), 1618, 1601, 1506, 1477, 1431, 1383, 1275, 1234, 1105, 1072, 850 cm^{-1}. ^{1}H NMR (DMSO-d_6 with TMS): δ 9.70 (s, 2H, OH), 7.91−7.93 (d, 2H), 7.34−7.36 (d, 8H), 7.08−7.18 (m, 8H), 6.87−6.90 (d, 2H), 1.70 (s, 6H, CH_3), 1.57 (s, 6H, CH_3). ^{13}C NMR (DMSO-d_6 with TMS): δ 166.6, 166.5, 162.7, 152.7, 151.7, 147.0, 141.1, 134.6, 128.6, 127.7, 125.8, 119.7, 118.1, 116.2, 111.6, 42.1, 41.1, 30.8, 30.6. Anal. Calcd for $C_{46}H_{34}N_2O_8$: C, 74.38; H, 4.61; N, 3.77%. Found: C, 74.04; H, 5.19; N, 3.78%.

Polyimide Thermal Conversion. Thin films of poly(amic acid) solution or soluble hydroxy-containing polyimide were cast from DMAc onto glass microscope slides. The films were dried under vacuum for 1 h at 25 °C, 1 h at 60 °C, and 1 h at 120 °C. Poly(amic acid) films were transformed to polyimides by heating for 1 h at 300 °C under vacuum or nitrogen. The hydroxy-containing polyimides were thermally converted to polybenzoxazoles by heating the films on the glass slides for 0.5−1 h between 350 and 500 °C under vacuum or nitrogen. The samples were cooled and immersed in water to release the films from the slides.

BPADA−DAPP Polyimide−Benzoxazole. IR (film): 2968 (aliphatic C−H), 1783, 1730 (C=O), 1492, 1479, 1384, 1275, 1241 cm^{-1}. Anal. Calcd for $C_{42}H_{28}N_2O_5$: C, 78.74; H, 4.41; N, 4.37%. Found: C, 78.75; H, 4.45; N, 4.12%.

BPDA−HAB Polybenzoxazole. Polyimide film was converted to polybenzoxazole by heating for 1 h at 500 °C under nitrogen; TGA 5 wt % loss in nitrogen occurred at 625 °C; no T_g or T_m was observed by DSC up to 500 °C. ^{13}C (CP/MAS): δ 163.2, 151.6, 141.4, 127.1, 108.5. IR (film): 3040 (Ar C−H), 1617, 1485, 1461, 1266, 1058, 828, 813 cm^{-1}. Anal. Calcd for $C_{26}H_{14}N_2O_2$: C, 80.82; H, 3.65; N, 7.25%. Found: C, 80.46; H, 3.76; N, 7.00%.

BPDA−APAF Polybenzoxazole. Anal. Calcd for $C_{29}H_{14}F_6N_2O_2$: C, 64.93; H, 2.63; N, 5.22%. Found: C, 62.25; H, 3.11; N, 4.94%.

BTDA−DAPP Polyimide−Benzoxazole. Anal. Calcd for $C_{28}H_{14}N_2O_4$: C, 76.01; H, 3.19; N, 6.33%. Found: C, 74.40; H, 3.32; N, 6.01%.

6FDA−DAPP Polyimide−Benzoxazole. Anal. Calcd for $C_{30}H_{14}F_6N_2O_3$: C, 63.84; H, 2.50; N, 4.96%. Found: C, 63.70; H, 2.39; N, 4.81%.

ODPA−APAF Polybenzoxazole. Polyimide film was converted to polybenzoxazole by heating for 1 h at 400 °C under vacuum. IR (film): 3074, 1735, 1601, 1558, 1481, 1236, 1138, 1051, 808 cm^{-1}. Anal. Calcd for $C_{29}H_{14}F_6N_2O_3$: C, 63.05; H, 2.55; N, 5.07%. Found: C, 62.94; H, 2.39; N, 5.03%.

BPADA−APAF Polybenzoxazole. Polyimide film was converted to polybenzoxazole by heating for 30 min at 400 °C under vacuum. IR (film): 2968, 1599, 1558, 1493, 1246 cm^{-1}. Anal. Calcd for $C_{44}H_{28}F_6N_2O_4$: C, 69.29; H, 3.70; N, 3.67%. Found: C, 69.16; H, 3.80; N, 3.87%.

***N*-(2-Hydroxyphenyl)phthalimide (1).** 2-Aminophenol (5.00 g, 45.8 mmol) was dissolved in *N*,*N*-dimethylacetamide (DMAc) (40 mL) and toluene (10 mL) in a 100 mL round-bottom flask fitted with a Dean-Stark trap, reflux condenser, and nitrogen purge. To the stirring contents at room temperature was added phthalic anhydride (6.79 g, 45.8 mmol). A small exotherm was observed during formation of the amic acid. The reaction was allowed to proceed at room temperature for 1 h and then refluxed for 4 h to remove the water of imidization as a toluene−water azeotrope. Excess toluene was then removed by distillation. After cooling, the flask contents were slowly poured into methanol/water (200 mL, 1:1 mixture by volume). The brown precipitate was collected by filtration, washed with water, and recrystallized from ethanol to give yellow crystals of **1**. The product was dried at 80 °C for 4 h in vacuo; yield 7.90 g (72%); mp 229−233 °C. ^{1}H NMR (DMSO-d_6 with TMS): δ 9.93 (s, 1H, OH), 7.96 (m, 2H), 7.87 (m, 2H), 7.34 (m, 2H), 7.06 (d, 1H), 6.95 (t, 1H). ^{13}C NMR (DMSO-d_6 with TMS): δ 167.3, 154.1, 134.6, 132.0, 130.5, 123.3, 119.3, 119.0, 116.7. Anal. Calcd for $C_{14}H_9NO_3$: C, 70.29; H, 3.79; N, 5.85%. Found: C, 70.34; H, 3.96; N, 5.86%.

***N*-(2-Deuteriohydroxyphenyl)phthalimide (2).** To a 125 mL Erlenmeyer flask containing 60 mL of acetone was added

1 (8.00 g, 33.4 mmol), and the mixture was heated to reflux with stirring to form a yellow solution. D_2O (5 mL) was added dropwise over 5 min. A precipitate formed near the end of addition. The acetone was allowed to boil off until the solution volume became 20 mL. The mixture was allowed to cool, and the solid was collected by filtration. The solid was placed back in the Erlenmeyer flask and the procedure repeated. The solid was again collected by filtration and then dried under vacuum for 3 h at 120 °C to give **2** as yellow crystals. Yield 4.88 g, (60%); mp 229−233 °C. The phenolic proton of **2** was found to be 84% D atom by ^{1}H NMR integration relative to the aromatic protons. ^{1}H NMR (DMSO-d_6 with TMS): δ 9.89 (s, 0.16H), 7.88−7.98 (m, 4H), 7.28−7.36 (m, 2H), 7.02−7.04 (d, 1H), 6.91−6.96 (t, 1H). ^{13}C NMR (DMSO-d_6 with TMS): δ 167.1, 153.8, 134.5, 131.8, 130.3, 123.2, 119.1, 118.7, 116.4.

2-(2-Methylphenyl)benzoxazole (3). A 125 mL three-neck, round-bottom flask was fitted with a mechanical stirrer and nitrogen atmosphere. To the flask was added 85 wt % *o*-phosphoric acid (25 g). The flask was immersed in a water bath at ambient temperature, and then phosphorus pentoxide (16 g, 112.7 mmol) was added to the flask with stirring. After the exotherm subsided (~5 min), the water bath was removed. To the warm, slightly viscous polyphosphoric acid was added *o*-toluic acid (5.00 g, 36.7 mmol). The reaction was heated to 90 °C for 15 min with an oil bath to give a yellow mixture. 2-Aminophenol (4.01 g, 36.7 mmol) was added to the flask to give a brown heterogeneous reaction mixture. The reaction was stirred for 1 h at 90 °C and then heated to 140 °C for 12 h. The resulting green solution was allowed to cool and then slowly poured into 300 mL of rapidly stirred water. The tan precipitate was collected by filtration, washed with water, and then dissolved in 50 mL of methylene chloride. The methylene chloride solution was extracted with 50 mL of 1 M NaOH followed by washing with 50 mL of water. Concentration of the methylene chloride solution to a solid residue, followed by sublimation of the residue at 140 °C (<1 mmHg), gave white crystals of **3**. Yield 6.06 g, (79%); mp 64−66 °C. ^{1}H NMR ($CDCl_3$ with TMS): δ 8.14 (m, 1H), 7.78 (m, 1H), 7.51 (m, 1H), 7.30 (m, 5H), 2.78 (s, 3H, Ar−CH_3). ^{13}C NMR ($CDCl_3$ with TMS): δ 163.2, 150.2, 142.1, 138.8, 131.7, 130.8, 129.8, 126.1, 125.9, 124.9, 124.3, 120.1, 110.4, 22.2.

2-(2-Carboxyphenyl)benzoxazole (4). A 250 mL three-neck, round-bottom flask fitted with a reflux condenser, heating mantle, and stir bar was charged with **3** (5.00 g, 23.9 mmol), KOH pellets (2.67 g, 47.8 mmol), pyridine (40 mL), and water (3 mL). With stirring, the contents of the flask were heated to a gentle reflux. Granular $KMnO_4$ (34.0 g, 215 mmol) was added in small portions through the top of the reflux condenser over a 2 h period. The solid was rinsed into the reaction flask with a few milliliters of water upon each addition. After a total of 5 h at reflux, the contents of the flask were allowed to cool. The reaction mixture was filtered through filter paper with aspiration to remove MnO_2. The resulting yellow-brown filtrate was diluted with 150 mL of water, placed in an ice/water bath, and stirred for 15 min. Unreacted **3** crystallized upon cooling and was collected by filtration. The filtrate was acidified with stirring at 0 °C by slow addition of 150 mL of 6 M HCl. The resulting white precipitate of **4** was collected by filtration, washed with water, and recrystallized from 40 mL of ethanol. Upon collecting by filtration and drying under vacuum for 4 h at 90 °C, **4** was obtained as white crystals. Yield 3.30 g (57%); mp 223−225 °C. ^{1}H NMR (DMSO-d_6 with TMS): δ 13.42 (s, 1H, COOH), 8.04 (m, 1H), 7.95 (m, 1H), 7.88 (m, 1H), 7.77 (m, 3H), 7.47 (m, 2H). ^{13}C NMR (DMSO-d_6 with TMS): δ 168.5, 162.2, 150.5, 141.4, 133.6, 131.4, 131.3, 130.3, 129.2, 126.1, 125.5, 124.7, 119.6, 110.9. Anal. Calcd for $C_{14}H_9NO_3$: C, 70.29; H, 3.79; N, 5.85%. Found: C, 70.18; H, 4.00; N, 5.74%.

2-(2-Bromophenyl)benzoxazole (5). To a 250 mL three-neck, round-bottom flask fitted with a mechanical stirrer and nitrogen purge was added 85 wt % *o*-phosphoric acid (100 g). The flask was submerged in an ambient temperature water bath. With stirring, phosphorus pentoxide (64 g, 450 mmol) was added to the flask in small portions over 5 min. After the exotherm subsided (10 min), the water bath was removed and replaced with an oil bath. The resulting poly(phosphoric acid) was heated to 90 °C, and then *o*-bromobenzoic acid (25.73 g, 128 mmol) was added to the flask. After 30 min of stirring at 90 °C, 2-aminophenol (13.97 g, 128 mmol) was added to the flask. The reaction mixture was heated at 140 °C for 12 h. The resulting dark green solution was allowed to cool and then poured slowly into 800 mL of rapidly stirred water. The orange solid that formed after 5 min was collected by filtration, washed with water, and sublimbed at 140 °C (<1 mmHg) to give light yellow crystals of **5**. Yield 29.79 g, (85%); mp 77−79 °C. ^{1}H NMR ($CDCl_3$ with TMS): δ 8.03 (m, 1H), 7.82 (m, 1H), 7.69 (m, 1H), 7.56 (m, 1H), 7.32 (m, 4H). ^{13}C NMR ($CDCl_3$ with TMS): δ 161.3, 150.5, 141.6, 134.6, 132.0, 131.9, 128.2, 127.3, 125.5, 124.6, 121.8, 120.4, 110.7.

2-(2-Deuteriophenyl)benzoxazole (6). A dry 50 mL two-neck, round-bottom flask fitted with a reflux condenser and nitrogen purge was charged with **5** (2.00 g, 7.30 mmol) and magnesium turnings (0.35 g, 14.40 mmol). Dry THF (10 mL) was added to the flask via syringe. To this stirred light-yellow solution at ambient temperature was added a crystal of iodine to give an orange solution. Within 10 min the orange color faded, indicating initiation of the reaction, and then the reaction color gradually progressed from light-yellow to green to dark brown. The reaction was allowed to stir at ambient temperature for a total of 1.5 h, at which time a purple color had formed. The flask was immersed in an ice/water bath and cooled to 0 °C. A solution of D_2O (0.15 g, 7.50 mmol) in THF (5 mL) was added dropwise with a constant pressure addition funnel over 10 min. A precipitate formed toward the end of addition. The reaction was allowed to warm to ambient temperature for 10 min, and then 1 M HCl (20 mL) was added. The aqueous phase was saturated with NaCl while stirring for 10 min. The reaction mixture was filtered under aspiration to remove unreacted magnesium and undissolved salt. The upper brown organic phase was collected and concentrated to a solid residue. The residue was sublimed at 120 °C (<1 mmHg) to give light-tan crystals of **6**. Yield 1.05 g, (73%); mp 101−104 °C. ^{1}H NMR ($CDCl_3$ with TMS): δ 8.22 (m, 1H), 7.76 (m, 1H), 7.52 (m, 1H), 7.46 (d, 3H), 7.30 (m, 2H). ^{13}C NMR ($CDCl_3$ with TMS): δ 162.9, 150.7, 142.1, 131.4, 128.8, 128.7, 127.6, 127.3, 127.0, 125.0, 124.5, 120.0, 110.5.

Bisphthalimide of DAPP (7). Monomer DAPP (2.00 g, 10.0 mmol) was reacted with phthalic anhydride (2.96 g, 20.0 mmol) and isolated as described for the synthesis of **1**. The resulting light-brown solid was recrystallized from DMAc, collected by filtration, and dried at 120 °C for 4 h in vacuo to give a white powder. Yield 3.15 g (68%); mp 370−374 °C. ^{1}H NMR (DMSO-d_6 with TMS): δ 10.28 (s, 1H, OH), 8.01 (m, 4H), 7.92 (m, 6H), 7.65 (d, 2H), 7.46 (t, 2H), 7.34 (t, 1H). ^{13}C NMR (DMSO-d_6 with TMS): δ 167.2, 151.0, 138.1, 134.7, 132.2, 131.0, 129.5, 129.1, 127.4, 126.0, 123.5, 120.9. IR (KBr) 3188 (O−H), 1785, 1721 (C=O), 1700 (C=O, hydrogen bonded), 1368, 1354, 714 cm^{-1}. Anal. Calcd for $C_{28}H_{16}N_2O_5$: C,73.04; H, 3.50; N, 6.08%. Found: C, 72.85; H, 3.70; N, 5.96%.

Bisphthalimide of HAB (8). Monomer HAB (5.00 g, 23.1 mmol) was reacted with phthalic anhydride (6.85 g, 46.2 mmol) and isolated as described for the synthesis of **1**. The brown solid was collected by filtration, washed with water and methanol, and recrystallized from DMAc. The light-brown crystals were collected by filtration, washed with acetone, and dried at 120 °C for 4 h in vacuo. Yield 7.61 g (69%); mp 380−384 °C with gas evolution. ^{1}H NMR (DMSO-d_6 with TMS): δ 10.12 (s, 2H, OH), 7.91−8.01 (m, 8H), 7.39−7.41 (d, 2H), 7.20−7.24 (m, 4H). ^{13}C NMR (DMSO-d_6 with TMS): δ 167.3, 154.4, 142.2, 134.8, 132.1, 131.0, 123.5, 118.7, 117.9, 114.9. IR (KBr): 3374 (O−H), 1785, 1725, 1703 (C=O), 1497, 1385, 719 cm^{-1}. Anal. Calcd for $C_{28}H_{16}N_2O_6$: C, 70.59; H, 3.38; N, 5.88%. Found: C, 70.51; H, 3.70; N, 5.67%.

Liquid Phase Thermal Conversion of 1. A glass tube sealed at one end (5 mm i.d. × 7 mm o.d. × 100 mm) was charged with **1** (0.500 g, 2.090 mmol). The contents of the vertical tube were heated for 30 min at 400 °C under nitrogen. Gas evolution was observed in the molten yellow liquid beginning at 350 °C. Colorless needle crystals formed in the upper cold portion of the tube. The crystals were collected and identified by ^{1}H NMR, ^{13}C NMR, and gas chromatography as phthalic anhydride (**9**) (mp 127−129 °C). After cooling, the black, solidified contents in the lower portion of the tube were dissolved in 15 mL of chloroform. Column chromatography of this solution on silica gel with chloroform mobile phase, followed by concentration and drying of the eluent fraction for 2 h at ambient temperature in vacuo, afforded 2-phenylbenzoxazole (**10**) as light-yellow crystals. Yield 0.077 g, (18%); mp 100−103 °C. ^{1}H NMR ($CDCl_3$ with TMS): δ 8.24 (t, 2H), 7.77 (m, 1H), 7.56 (m, 1H), 7.51 (d, 3H), 7.33 (m, 2H). ^{13}C NMR ($CDCl_3$ with TMS): δ 163.0, 150.75, 142.1, 131.5, 128.9, 127.6, 127.2, 125.1, 124.6, 120.0, 110.6. Anal. Calcd for $C_{13}H_9NO$: C, 79.98; H, 4.65; N, 7.17%. Found: C, 79.72; H, 4.98; N, 7.27%. Continuing elution with 20:1 (v/v) chloroform/ethyl acetate mobile phase gave a solution which was highly fluorescent under 254 nm UV light. Concentration and drying of this fraction for 2 h at ambient temperature in vacuo gave 2,2′-*o*-phenylenebisbenzoxazole (**11**) as a brown crystalline solid. Yield 0.073 g (22%) based on 2 mol of **1** per mole of **11**; mp 177−180 °C (lit.[17] mp 174 °C). ^{1}H NMR (DMSO-d_6 with TMS): δ 8.16 (m, 2H), 7.87 (m, 2H), 7.74 (m, 2H), 7.58 (m, 2H), 7.40 (m, 4H). ^{13}C NMR (DMSO-d_6 with TMS): δ 161.5, 150.4, 141.2, 131.8, 131.0, 126.7, 125.8, 124.8, 120.0, 110.8. Anal. Calcd for $C_{20}H_{12}N_2O_2$: C, 76.91; H, 3.87; N, 8.97%. Found: C, 76.77; H, 4.00; N, 8.84%.

Vapor Phase Thermal Conversion of 1. A quartz tube (5 mm i.d. × 7 mm o.d. × 120 cm length) was fitted with two heating zones fabricated from coiled nickel−chromium resistance wire. Zone 1 (15 cm length) and zone 2 (70 cm length) were heated using variable resistors. The temperature in each zone was calibrated from ambient to 750 °C with a digital thermocouple. Zone 2 was packed with dry 4 Å molecular sieves. An NMR tube open on both ends (5 mm o.d. × 17 cm length) was charged with **1** (0.179 g, 0.752 mmol) and inserted into the quartz tube so that the sample was within heating zone 1. Another NMR tube open on both ends was inserted into the unheated end on the other side of the quartz tube. This NMR tube was placed in contact with the sieve packing. A vacuum pump and vacuum gauge were connected to the quartz tube at the end of zone 2. Zone 1 was connected to a dry nitrogen bleed. A vacuum was pulled on the reaction tube, and the nitrogen bleed was adjusted to give a pressure of 0.5 mmHg in the tube. Zone 2 was now heated and allowed to equilibrate at 400 °C for 10 min. The sample in zone 1 was then heated to 230 °C. Over a 1 h period, the sample in zone 1 completely sublimed away. The nitrogen bleed encouraged sublimation to proceed toward zone 2. During heating, a new, white crystalline product collected in the cool NMR tube beyond zone 2. After the apparatus was cooled, the crystalline product was collected and identified by GC and NMR as pure 2-phenylbenzoxazole (**10**). Yield 0.146 g (83%); mp 101−103 °C. ^{1}H NMR ($CDCl_3$ with TMS): δ 8.20−8.23 (m, 2H), 7.74−7.76 (m, 1 H), 7.49−7.52 (m, 1H), 7.44−7.46 (t, 3H), 7.28−7.32 (m, 2H). ^{13}C NMR ($CDCl_3$ with TMS): δ 162.9, 150.6, 142.0, 131.4, 128.7, 127.5, 127.1, 125.0, 124.5, 119.9, 110.5.

Thermal Rearrangement of 7. A glass tube (5 mm i.d. × 7 mm o.d. × 180 mm) open on both ends was charged at one end with **7** (0.0890 g, 0.1933 mmol). A nitrogen flow of 40 mL/min through the horizontally suspended tube was introduced at the end containing the sample. The sample was heated for 30 min at 400 °C using a resistance wire wrapped around the tube in the sample region. Gas evolution was observed when the reaction mixture became molten (ca. 370 °C). A yellow solid sublimed to the cooler portion of the tube. After cooling the tube, the yellow solid was removed, recrystallized from DMAc and dried in vacuo at 120 °C for 4 h to give **12** as light-yellow crystals. Yield 0.0203 g (25%); mp 298−300 °C. ^{1}H NMR (DMSO-d_6 with TMS): δ 8.15−8.21 (m, 3H), 8.06−8.10 (m, 2H), 7.95−8.00 (m, 2H), 7.90 (d, 1H), 7.74−7.78 (d, 2H), 7.41−7.62 (m, 6H). ^{13}C NMR (DMSO-d_6 with TMS): δ 166.2, 163.2, 145.1, 143.7, 139.1, 137.9, 135.1, 132.4, 131.6, 129.4, 129.1, 127.8, 127.6, 127.1, 125.8, 124.1, 123.9, 118.0, 115.8. IR (KBr): 3063, 1725 (C=O), 1477, 1381, 713, 700 cm^{-1}. Anal. Calcd for $C_{27}H_{16}N_2O_3$: C, 77.87; H, 3.87; N, 6.73%. Found: C, 77.66; H, 4.14; N, 6.71%.

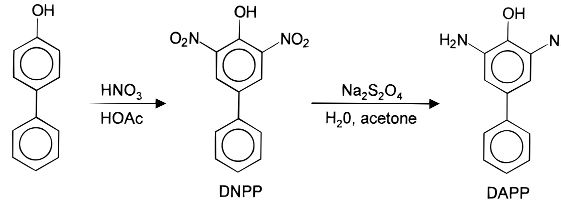

Figure 1. Synthesis of 2,6-diamino-4-phenylphenol (DAPP) from 4-phenylphenol.

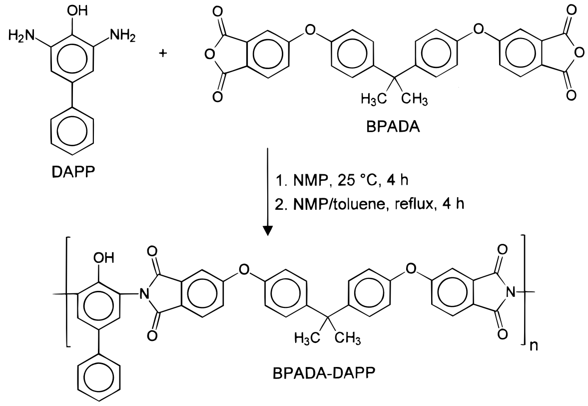

Figure 2. Synthesis of BPADA−DAPP polyimide via conventional two-step solution reaction. Polyamic acid formation at ambient temperature followed by thermal solution imidization.

Thermal Rearrangement of 8. The thermal rearrangement of **8** was conducted as described for **7** . Compound **8** (0.1112 g, 0.2334 mmol) was heated for 30 min at 400 °C under nitrogen flow. The resulting yellow crystalline solid which collected in the cold portion of the tube was recrystallized from DMAc. The product was collected by filtration and dried in vacuo at 120 °C for 4 h to give bisbenzoxazole (**13**) as white, platelike crystals. Yield 0.0039 g (5%); mp 264−267 °C. ^{1}H NMR ($CDCl_3$ with TMS): δ 8.28−8.31 (m, 4H), 7.87 (s, 1H), 7.84−7.85 (t, 3H), 7.68 (s, 1H), 7.64−7.65 (d, 1H), 7.55−7.57 (m, 6H). ^{13}C NMR ($CDCl_3$ with TMS): δ 163.7, 151.5, 141.7, 138.6, 131.7, 129.0, 127.7, 127.1, 124.5, 120.1, 109.4. IR (KBr) 3059, 1619, 1548, 1052, 821, 701, 689 cm^{-1}. Anal. Calcd for $C_{26}H_{16}N_2O_2$: C, 80.40; H, 4.15; N, 7.21%. Found: C, 80.43; H, 4.25; N, 6.97%. Repeating the thermal rearrangement of **8** in the presence of copper(I) iodide (5 mol %) resulted in a 22% yield of bisbenzoxazole (**13**) after recrystallization and drying.

Results and Discussion

Polymers. Previous work in our group led to an unexpectedly facile synthesis of 2,6-diamino-4-phenylphenol (DAPP) in two steps from the readily available 4-phenylphenol (Figure 1). Although the synthesis of DAPP was straightforward, this compound proved to be quite susceptible to oxidation, and therefore it was used in polymerization reactions immediately after preparation. In our efforts to obtain soluble and/or processable polyimides, DAPP was reacted with bisphenol A dianhydride (BPADA**)** in the normal two-step process using thermal solution imidization to give the novel polyimide shown in Figure 2. During routine thermogravimetric analysis of the BPADA−DAPP polyimide in nitrogen, a well-defined weight loss comprising 6.3% of the sample weight was observed between 375 and 500 °C followed by the onset of catastrophic degradation at 525 °C (Figure 3). This step loss implied conversion to some more stable structure through a process not immediately obvious. In an effort to elucidate both the new structure and process, we first confirmed the weight loss.

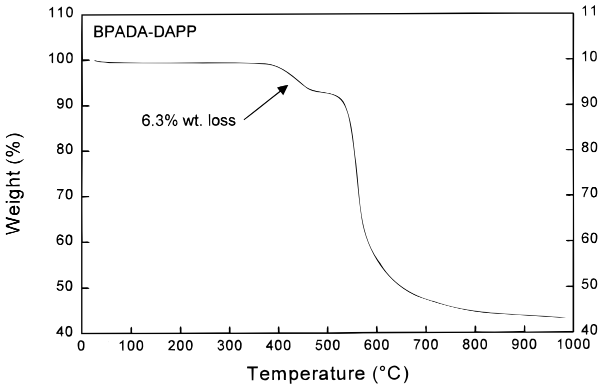

Figure 3. Thermogravimetric analysis of BPADA−DAPP polyimide (in nitrogen) showing well-defined 6.3% weight loss between 350 and 500 °C.

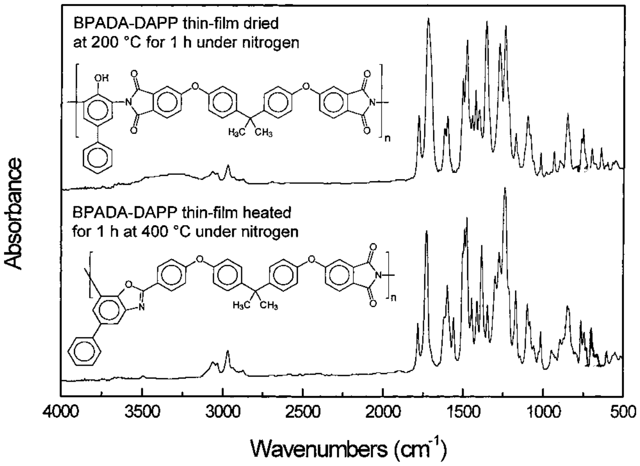

Figure 4. Infrared spectra of polymer thin films of BPADA−DAPP polyimide dried for 1 h at 200 °C under nitrogen (upper trace) and heated for 1 h at 400 °C under nitrogen (lower trace).

A thin film of BPADA−DAPP, solution cast form chloroform, was heated isothermally for 1 h under nitrogen atmosphere in the temperature range of the 6.3% weight loss (ca. 400 °C). The resulting film sample was insoluble yet swelled in the casting solvent, indicating some degree of cross-linking or crystallization had occurred. Infrared spectra of the BPADA−DAPP film sample were obtained before heating (polyimide film dried at 200 °C for 1 h) and after heating at 400 °C (Figure 4). The characteristic O−H stretch at 3400 cm^{-1} for this hydroxy-containing polyimide (upper spectrum) disappeared in the film sample heated at 400 °C (lower spectrum). Symmetric and asymmetric carbonyl stretches at 1780 and 1730 cm^{-1} were still visible in both spectra, indicating that the sample heated to 400 °C still contained some imide linkages. The BPADA−DAPP polyimide contains two imide linkages per pendent hydroxyl group. If the hydroxyl group undergoes intramolecular reaction with one of the imide linkages at elevated temperature, this will leave intact one unreacted imide linkage per repeat unit.

At this point, the project was directed toward elucidating the molecular origin of the weight loss, and carbon dioxide was proposed as a possible small molecule condensate eliminated from the polymer backbone by thermal decarboxylation. Theoretical weight loss of carbon dioxide from the BPADA−DAPP polyimide is 6.4%, a value which agrees well with the observed value of 6.3%. A benzoxazole was proposed as one possible, thermally stable structure formed upon decarboxylation. The project was then extended to additional polymer synthesis and characterization to confirm generality of this novel process, especially to hydroxy-containing polyimides which possessed equal numbers of hydroxyl and imide groups. Thermal conversion of polymers of this type should result in the exclusive formation of polybenzoxazoles, thus simplifying infrared characterization. The thermal conversion of several hydroxy-containing imide model compounds was also studied, because the soluble products from small molecule reactions are more amenable to solution characterization.

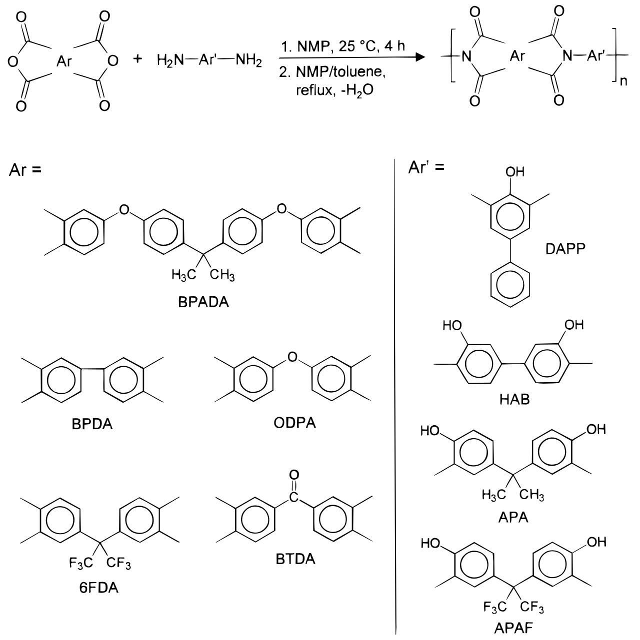

Figure 5. Overall synthesis and structures of hydroxy-containing polyimides.

The series of hydroxy-containing polyimides was prepared by the conventional two-step solution condensation of dianhydrides with bis-*o*-aminophenols as shown in Figure 5. Upon thermal dehydration in solution, polyimides derived from less flexible dianhydrides, such as BPDA, became insoluble. In cases of polyimide insolubility, films were cast from the poly(amic acid) solutions and thermally converted to the corresponding polyimdes at 300 °C under vacuum or nitrogen. Polyimide solubility increased as the anhydride functionality became more flexible. Hexafluoroisopropylidene-containing polyimides displayed good solubility in a range of organic solvents, some even being soluble in acetone. Most of the polymers in the series showed solubility in aqueous 1 M sodium hydroxide, although little increase in viscosity was observed upon dissolution perhaps due to backbone hydrolysis. The resulting solutions became darker in color, presumably due to phenoxide ion formation. The solubility characteristics of the polyimides are listed in Table 1.

Number-average and weight-average molecular weights relative to polystyrene standards were obtained by SEC on THF-soluble polyimides. The molecular weight data and intrinsic viscosity results are shown in Table 2. Number-average molecular weights ranged from 3800 to 180 000. The lower molecular weight polymers 6FDA−DAPP ($M_n = 3800$, $M_w = 10\,400$) and ODPA−APAF ($M_n = 4300$, $M_w = 15\,300$) displayed bimodal molecular weight distributions. Polyimides containing BPDA were insoluble in all organic solvents tested. The intrinsic

Table 1. Solubility Characteristics of Hydroxy-Containing Polyimides[a]

polymer	1 M NaOH	methanol	acetone	THF	$CHCl_3$	toluene	DMSO	DMAc	NMP
BPDA−HAB	−	−	−	−	−	−	−	−	−
BPDA−APAF	+	−	−	−	−	−	−	−	−
BPDA−APA	+	−	−	−	−	−	−	−	−
BTDA−DAPP	+	−	−	−	−	−	+	+	+
6FDA−DAPP	+	−	+	+	−	−	+	+	+
ODPA−APAF	+	−	+	+	−	−	+	+	+
ODPA−APA	+	−	−	−	−	−	+	+	+
BPADA−DAPP	−	−	−	+	+	−	+	+	+
BPADA−APAF	+	−	+	+	−	−	+	+	+
BPADA−APA	+	−	−	+	−	−	+	+	+

[a] Symbols: +, soluble; −, insoluble.

Table 2. Molecular Weight (SEC) and Intrinsic Viscosity Data for Hydroxy-Containing Polyimides

polymer	M_n[a]	M_w	peak max	$[\eta]$[b] (dL/g)
BPDA−HAB	ins[d]	ins	ins	0.82[c]
BPDA−APAF	ins	ins	ins	ins
BPDA−APA	ins	ins	ins	ins
BTDA−DAPP	ins	ins	ins	0.50
6FDA−DAPP	3800	10 400	22 700	0.30
ODPA−APAF	4300	15 300	29.900	0.42
ODPA−APA	ins	ins	ins	0.53
BPADA−DAPP	180 000	316 400	282 400	1.63
BPADA−APAF	40 500	74 000	63 300	0.44
BPADA−APA	45 100	100 800	87 300	0.86

[a] Molecular weights relative to polystyrene standards in THF. [b] Intrinsic viscosity measured in DMAc at 30 °C. [c] Intrinsic viscosity of BPDA−HAB poly(amic acid). [d] ins = insoluble.

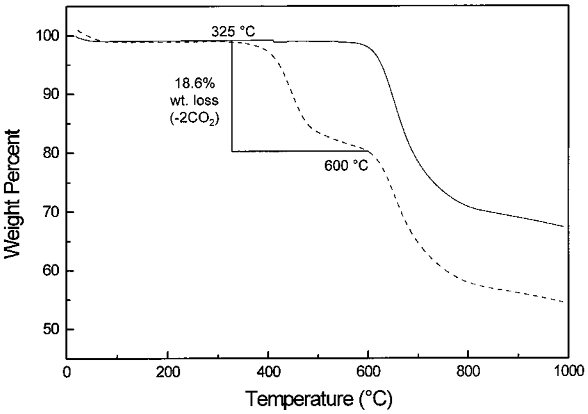

Figure 6. Thermogravimetric analysis in nitrogen (heating rate 20 °C/min) of BPDA−HAB polyimide (dashed line) and the same polymer after heating isothermally for 1 h at 500 °C under nitrogen (solid line).

viscosity of BPDA−HAB (0.82 dL/g) was determined on the poly(amic acid). Intrinsic viscosity measurements in DMAc correlated well with the estimated molecular weight values obtained by SEC. All of the soluble polyimides displayed molecular weights sufficient for film formation on solution casting.

The most in-depth study of polyimide thermal conversion to polybenzoxazole was conducted on the BPDA−HAB polymer system. The BPDA−HAB polyimide was prepared via thermal imidization of solution-cast (DMAc) thin films of the polyamic acid by heating for 1 h under nitrogen at 300 °C. Thermogravimetric analysis of the BPDA−HAB polyimide in nitrogen (Figure 6) revealed a well-defined weight loss between 325 and 600 °C which comprised 18.6% of the sample weight. Calculations showed that expulsion of 2 mol of carbon dioxide per repeat unit would exactly account for this weight loss. Heating of a yellow BPDA−HAB polyimide film for 1 h under nitrogen in the region of weight loss (ca. 500 °C, dashed line, Figure 6) gave a purple-brown film. TGA testing of this film under nitrogen showed that the temperature for 5% weight loss increased to 625 °C (solid line in Figure 6). The inherent thermal stability of the material obtained after the 18.6% weight loss is also consistent with conversion to a polybenzoxazole above ∼350 °C. The proposed sequence is shown in Figure 7, where the hydroxy−imide rearranges to a carboxy−benzoxazole intermediate followed by decarboxylation above 350 °C to give the fully aromatic benzoxazole product. The complete reaction sequence for the thermal formation of polybenzoxazole beginning with BPDA−HAB poly(amic acid) is shown in Figure 8. Coupled TGA/FTIR was conducted on the BPDA−HAB polyimide to determine the composition of off-gases during thermal conversion. The infrared spectra of the off-gas generated upon heating BPDA−HAB polymide under nitrogen flow (80 cm^3/min) at a heating rate of 20 °C/min are shown in Figure 9. Carbon dioxide evolution is detected from the sample beginning at approximately 350 °C. Maximum gas evolution for this

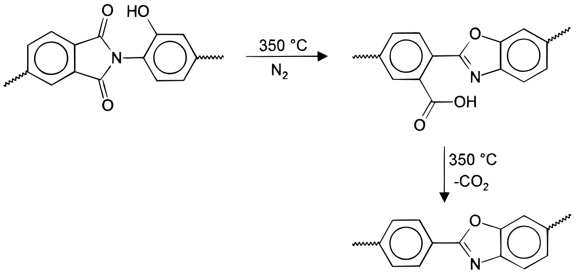

Figure 7. Proposed reaction for thermal conversion of hydroxy−imides to benzoxazoles.

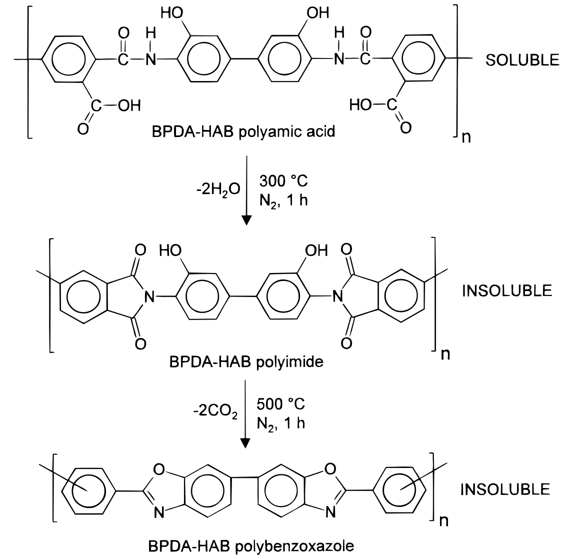

Figure 8. Thermal imidization of BPDA−HAB polyamic acid at 300 °C and subsequent thermal conversion to aromatic polybenzoxazole at 500 °C under nitrogen.

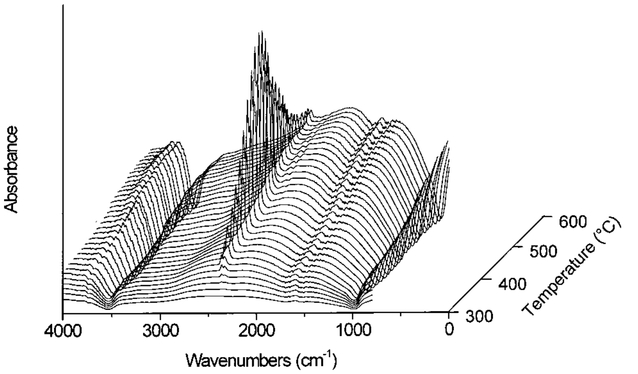

Figure 9. Time-slice gas-phase FTIR spectra of off-gas generated during thermogravimetric analysis of BPDA−HAB polyimide in nitrogen.

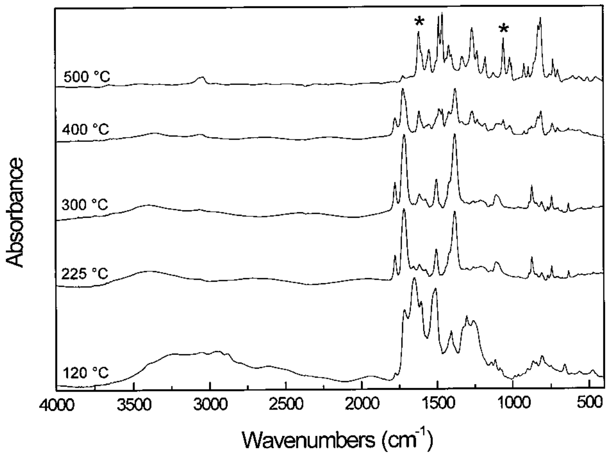

Figure 10. FTIR spectra (thin films) of BPDA−HAB polyamic acid after heating for 1 h under nitrogen at indicated temperatures.

sample occurred at 450 °C and then tapered off to near zero by 600 °C. No other volatile products were detected in the IR spectra, suggesting few if any side reactions occurred.

Thermal conversion of hydroxy-containing polyimide to polybenzoxazole was also monitored by FTIR. Thin-film samples of BPDA−HAB poly(amic acid) were heated under nitrogen atmosphere for 1 h at 120, 225, 300, 400, and 500 °C. The IR spectra of these samples are shown in Figure 10. Cyclization of the BPDA−HAB poly(amic acid) to the polyimide clearly occurred at 225 °C as seen by the appearance of characteristic imide carbonyl peaks at 1776 cm^{-1} (symmetric C=O stretching) and 1716 cm^{-1} (asymmetric C=O stretching). The hydroxy-containing polyimide structure remained stable to 300 °C but began to rearrange when heated to 400 °C, as evidenced by benzoxazole ring stretches (*) at 1617 and 1058 cm^{-1}. Almost complete conversion to the aromatic polybenzoxazole was observed at 500 °C, with disappearance of the OH stretch at 3400 cm^{-1} and only a small carbonyl absorbance remaining at 1716 cm^{-1}. Solid-state ^{13}C NMR spectra were obtained on samples of BPDA−HAB poly(amic acid) that had been heated for 1 h each at 300 and 500 °C (Figure 11). A peak for imide carbonyls at 167 ppm (a) is present in the upper trace of the hydroxy-containing polyimide formed at 300 °C. Heating at 500 °C results in disappearance of the carbonyl peak at 167 ppm and subsequent formation of characteristic benzoxazole resonances at 109 and 163 ppm (lower trace). The peak at 109 ppm (b) is attributed to the carbon ortho to the heterocyclic oxygen while the peak at 163 ppm (c) is diagnostic of the quaternary carbon (2-position) of the benzoxazole ring.

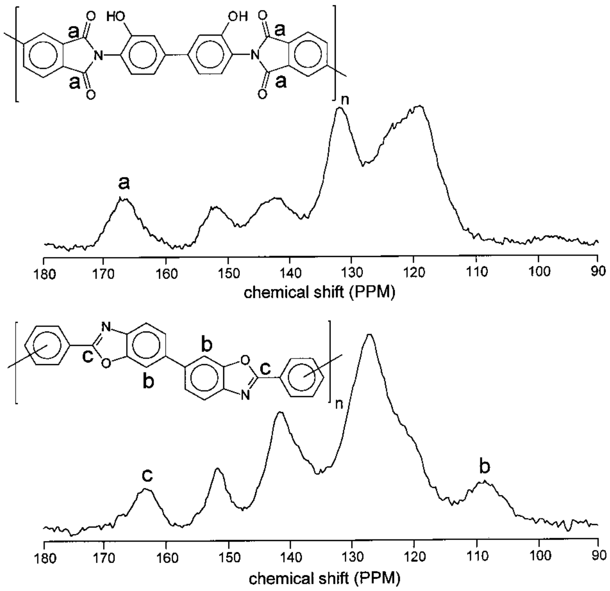

Figure 11. Solid-state ^{13}C CP/MAS NMR of BPDA−HAB polyimide (upper trace) and polybenzoxazole thermal conversion product (lower trace).

Table 3. Elemental Analysis Results for the Hydroxy-Containing Polyimides

	C (%)		H (%)		N (%)	
polyimide	calcd	found	calcd	found	calcd	found
BPDA−HAB	70.89	70.64	2.97	3.18	5.90	5.94
BPDA−APAF	59.63	59.49	2.26	2.21	4.49	4.60
BPDA−APA	72.09	70.35	3.90	5.12	5.42	5.99
BTDA−DAPP	71.61	71.36	2.90	3.07	5.76	5.55
6FDA−DAPP	61.19	60.96	2.32	2.22	4.60	4.55
ODPA−APAF	58.14	56.17	2.20	2.76	4.37	4.16
ODPA−APA	69.62	69.70	3.79	4.04	5.26	5.26
BPADA−DAPP	75.43	75.74	4.12	4.32	4.09	3.85
BPADA−APAF	64.95	65.09	3.32	3.46	3.29	3.26
BPADA−APA	74.38	74.04	4.61	5.19	3.77	3.78

Elemental analysis results confirmed the chemical compositions of the polyimides (Table 3), with acceptable agreement (±0.3%) for all polyimides except BPDA−APA, ODPA−APAF, and BPADA−APA. Results of small-angle X-ray scattering (SAXS) indicated a completely amorphous structure for the BPDA−HAB-derived aromatic polybenzoxazole in contrast to highly crystalline all-para, all-aromatic PBO.[18,19] The lack of crystallinity in the current system may be due to a combination of meta- and para-linked species which would give a more disordered structure. This decrease in crystallinity has been observed for polybenzoxazoles based on 2,2-bis(3-amino-4-hydroxyphenyl)propane copolymerized with iso- and terephthaloyl chlorides. Crystallinity decreased dramatically as the incorporation of meta-oriented isophthaloyl species increased.[20]

The thermal stability results in air and nitrogen for the polyimide series are listed in Table 4. The temperatures for 5% weight loss in air ranged from 353 to 463 °C, and the temperatures for 5% weight loss in nitrogen were from 346 to 456 °C. Similar thermal stabilities in both air and nitrogen are attributed to the onset of the thermal conversion reaction at 350 °C. In all cases, the theoretical weight loss of carbon dioxide from the polyimides is greater than 5%. Generally, polyimides containing APA displayed the lowest thermal stability in air and nitrogen. Char yields in nitrogen at 1000 °C

Table 4. Thermal Properties of Hydroxy-Containing Polyimides

polymer	T_g[a]	TGA 5% wt loss (°C)[b] air	N_2	char yield at 100 °C in N_2 (%)
BPDA−HAB	c		422	49
BPDA−APAF	354	388	387	52
BPDA−APA	344	353	346	35
BTDA−DAPP	341	455	446	54
6FDA−DAPP	329	463	456	51
ODPA−APAF	295	397	400	45
ODPA−APA	268	391	404	25
BPADA−DAPP	258	444	438	43
BPADA−APAF	251	399	395	48
BPADA−APA	238	380	405	25

[a] Heating rate of 10 °C/min in N_2; T_g reported as inflection point of trace. [b] Heating rate of 20 °C/min. [c] nd = none detected up to 500 °C.

Table 5. Calculated versus Found Carbon Dioxide Weight Loss (in %) from APAF and APA-Containing Polyimides by Thermogravimetric Analysis in Nitrogen

polyimide	CO_2 wt loss calcd	wt loss found (350−500 °C)	wt loss diff [found − calcd]
BPDA−APAF	14.1	13.2	−0.9
ODPA−APAF	13.7	14.0	0.3
BPADA−APAF	10.4	12.9	2.5
BPDA−APA	17.0	41.3	24.3
ODPA−APA	16.6	49.6	33.0
BPADA−APA	11.9	24.8	12.9

Table 6. Elemental Analysis Results for the Polybenzoxazoles

polybenz-oxazole	C (%) calcd	C (%) found	H (%) calcd	H (%) found	N (%) calcd	N (%) found
BPDA−HAB	80.82	80.46	3.65	3.76	7.25	7.00
BPDA−APAF	64.93	62.25	2.63	3.11	5.22	4.94
BPDA−APA						
BTDA−DAPP	76.01	74.40	3.19	3.32	6.33	6.01
6FDA−DAPP	63.84	63.70	2.50	2.39	4.96	4.81
ODPA−APAF	63.05	62.94	2.55	2.39	5.07	5.03
ODPA−APA						
BPADA−DAPP	78.74	78.75	4.41	4.45	4.37	4.12
BPADA−APAF	69.29	69.16	3.70	3.80	3.67	3.87
BPADA−APA						

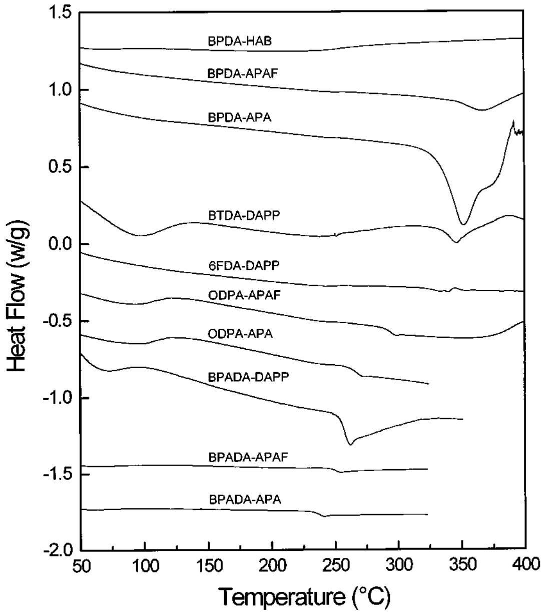

Figure 12. DSC thermograms for the polyimide series obtained at a heating rate of 10 °C/min.

ranged from 25% to 54% for the series. The relatively low char yield values are associated with the additional weight loss of carbon dioxide from the polymers during heating. Char yield values for the APA-containing polyimides were found to be the lowest, with values from 25% to 35%. TGA traces for all of the polyimides, except the APA-containing polyimides, showed a well-defined step weight loss between approximately 350 and 500 °C, which corresponds well with the calculated weight loss of CO_2 from the polymers over this temperature range.

Table 5 compares the actual CO_2 weight loss between 350 and 500 °C with the calculated weight loss for polyimides containing APAF. Good agreement is seen between the actual and theoretical CO_2 with loss values. In contrast, analogous polyimides containing APA did not display the step weight loss between 350 and 500 °C under nitrogen. Rather, these polyimides decomposed catastrophically above 400 °C. The measured and calculated CO_2 weight loss values for the APA-containing polyimides is also shown in Table 5. It should be noted that the measured weight loss between 350 and 500 °C was 2−3 times greater for these materials. The inability of APA-containing polyimides to undergo the thermal conversion reaction under inert atmosphere hints at some inherent instability for this particular bisaminophenol. The polyimides, with the exception of the APA-containing polymers, were thermally converted to polybenzoxazoles by heating for 1 h between 400 and 500 °C under nitrogen. Elemental analysis results support the formation of polybenzoxazoles in most cases as shown in Table 6.

The DSC traces for the polymer series are shown in Figure 12. Glass transition temperatures ranged from 238 to 354 °C and are listed in Table 4. No glass transition was observed for the rigid BPDA−HAB polyimide up to 500 °C, a temperature at which thermal conversion to the polybenzoxazole was occurring. Indeed, it proved difficult to get accurate glass transition temperature measurements for the more rigid polyimides in the series. The glass transition temperatures often approached the onset temperature of thermal conversion to polybenzoxazoles at approximately 350 °C, thus obscuring the transition. The rigid BPDA−HAB polyimide required heating for 1 h at 500 °C under nitrogen for near complete conversion to polybenzoxazole to occur as seen in the IR traces in Figure 10. Heating the BPDA−HAB polyimide for 1 h at 400 °C resulted in only slight conversion to polybenzoxazole, as imide carbonyl peaks at 1776 and 1716 cm^{-1} remained very prominent in the IR trace. Solution-cast films of hydroxy-containing polyimides with lower glass transition temperatures were produced in order to determine whether polymer chain flexibility allows thermal conversion to polybenzoxazoles at lower temperatures. Thin films of BPADA−APAF (T_g = 251 °C) and ODPA−APAF (T_g = 295 °C) polyimides were cast from THF solution onto glass microscope slides. The films were thermally converted to polybenzoxazoles by heating for 30 min at 400 °C under vacuum. Comparisons of the infrared spectra of the polyimides and resulting polybenzoxazoles are shown in Figures 13 and 14 for the BPADA−APAF- and ODPA−APAF-based polymers, respectively. As seen in the IR traces, thermal conversion of the lower glass transition temperature polyimides to polybenzoxazoles was virtually complete, as evidenced by the loss of the O−H stretch of the polyimides at 3400 cm^{-1}. The diminished intensity of the imide carbonyl absorptions, especially for the BPADA−APAF polyimide shown in Figure 13, also indicates that conversion to polybenzoxazole was nearly complete

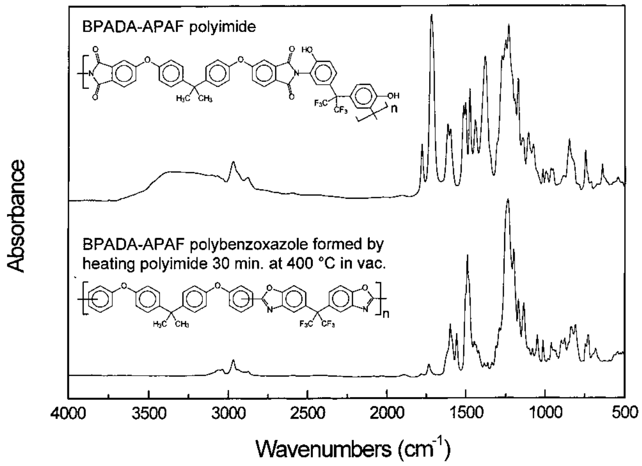

Figure 13. Infrared spectra of BPADA–APAF polyimide (upper trace) and polybenzoxazole from the thermal conversion of BPADA–APAF polyimide at 400 °C for 30 min under vacuum (lower trace).

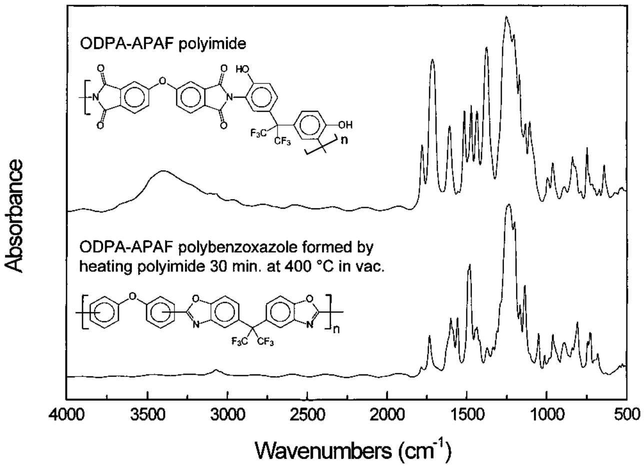

Figure 14. Infrared spectra of ODPA–APAF polyimide (upper trace) and polybenzoxazole from the thermal conversion of ODPA–APAF polyimide at 400 °C for 30 min under vacuum (lower trace).

after 30 min at 400 °C. The conversion of the BPADA–APAF and ODPA–APAF polyimides to polybenzoxazoles was more efficient than the BPDA–HAB polyimide at 400 °C. This suggests that polyimides with high glass transition temperatures (i.e., above 350 °C, the temperature at which thermal conversion begins to occur) do not have enough molecular mobility for rearrangement and decarboxylation to occur efficiently. The more flexible hydroxy-containing polyimides, with lower glass transition temperatures, undergo thermal conversion at a faster rate and lower temperature. This may be useful as an alternative processing technique for the production of polybenzoxazoles that are difficult to obtain by other routes.

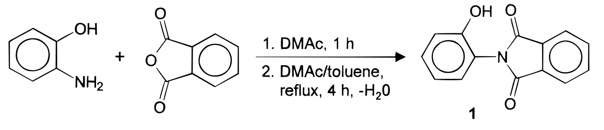

Figure 15. Synthesis of *N*-(2-hydroxyphenyl)phthalimide (**1**).

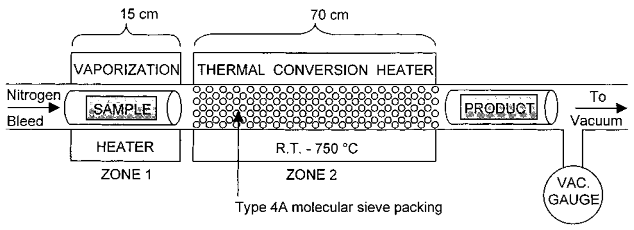

Figure 16. Apparatus for the vapor-phase thermal conversion of hydroxy–imide model compounds to benzoxazoles.

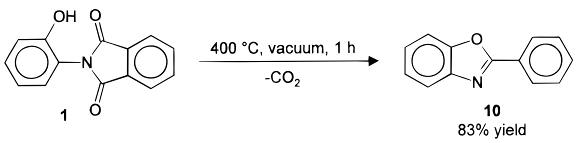

Figure 17. Thermal conversion of *N*-(2-hydroxyphenyl)phthalimide (**1**) to 2-phenylbenzoxazole (**10**) in the vapor phase.

Model Compounds. To further evaluate details of the thermal conversion reaction, model compounds were synthesized that mimic the hydroxy–imide portion of the polyimide backbone and gave products that were soluble after thermolysis, thus facilitating characterization. The first and simplest model hydroxy–imide examined was *N*-(2-hydroxyphenyl)phthalimide (**1**), prepared by the reaction of phthalic anhydride with 2-aminophenol in DMAc as shown in Figure 15. The synthesis of **1** followed the same two-step procedure used for polyimide formation (i.e., formation of the amic acid at ambient temperature followed by solution imidzation via removal of water as the toluene/water azeotrope). Pure **1** was obtained in 72% yield after recrystallization from ethanol.

The thermal conversion of **1** to benzoxazole was conducted in the vapor phase under vaccum and liquid phase in nitrogen, both at 400 °C. Interestingly, different reaction products were obtained from the vapor-phase and liquid-phase reactions. Thermolysis of **1** in the vapor phase was performed in a heated quartz tube. The vapor-phase thermal conversion apparatus is shown in Figure 16. Compound **1** was placed in sample zone 1, the apparatus was evacuated, and nitrogen was bled into the end of zone 1 to achieve a pressure of 0.5 mmHg in the system. Zone 2, packed with dry 4 Å molecular sieves, was heated and equilibrated at 400 °C. The temperature in zone 1 was adjusted to allow sublimation of **1** through zone 2 at 400 °C. After 1 h of sublimation, a new crystalline product collected in the cool portion of the apparatus aft of zone 2. The product, collected in 83% yield, was identified as pure 2-phenylbenzoxazole (**10**) by GC and NMR. The thermal conversion reaction of **1** to form **10** is shown in Figure 17.

The thermal conversion of **1** was repeated in the liquid state by simple heating to 400 °C in a vertically suspended glass tube under nitrogen. During heating, gas evolution was observed in the molten yellow liquid beginning at 350 °C, and colorless needle crystals gradually formed in the upper cold portion of the tube. After heating for 30 min, the resulting black contents at the bottom of the tube were allowed to cool and solidify. The colorless needle crystals at the top of the tube were collected and identified as phthalic anhydride (**9**) by GC and NMR (mp 127–129 °C). Column chromatography on a chloroform solution of the black solid (silica gel with chloroform mobile phase) followed by concentration and drying of the eluent gave 18% of 2-phenylbenzoxazole (**10**). Gas chromatography, NMR, and elemental analysis results confirmed the formation of **10**. Continuing elution of the column with 20:1 (v/v) chloroform/ethyl acetate resulted in the collection of an

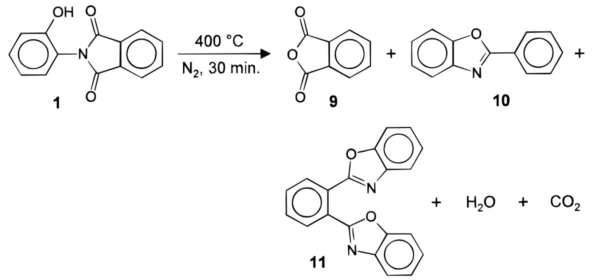

Figure 18. Products identified from the thermal conversion of *N*-(2-hydroxy phenyl)phthalimide (**1**) in the liquid state at 400 °C in nitrogen.

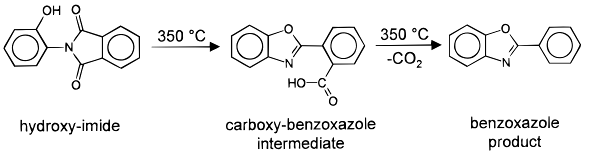

Figure 19. General scheme for the thermal conversion of hydroxy—imides to benzoxazoles showing proposed carboxy—benzoxazole intermediate.

eluent fraction that was highly fluorescent under 254 nm UV light. Concentration and drying of this fraction afforded 22% of 2,2′-*o*-phenylenebisbenzoxazole (**11**). Water was also apparently formed as a product of the thermal conversion reaction in the liquid state, its presence being detected by GC. The only other identified component of the thermolysis reaction was unreacted starting material (**1**). The products identified from the thermal conversion of **1** in the liquid phase are shown in Figure 18.

The multiple products identified in the liquid-state reaction indicate that intermolecular reactions are occurring. These results are not observed in the vapor-phase thermal conversion where exclusive formation of 2-phenylbenzoxazole suggests a purely intramolecular reaction. Results from the polyimide thermal conversions more closely resemble the vapor phase reaction of **1** to form pure 2-phenylbenzoxazole, in that only carbon dioxide was detected evolving from the polyimide samples during heating, and solid-state NMR, TGA-FTIR, and elemental analysis results support the formation of polybenzoxazoles. This seems to indicate that the low molecular motion of the polyimide chains favors intramolecular reaction (benzoxazole formation), whereas intermolecular reactions become significant during thermal conversion of model compound **1** in the molten state where molecular motion is much greater.

While studying the polyimide and model compound thermal conversion reactions, it was found that at least a temperature of 350 °C was necessary to convert the hydroxy—imides to benzoxazoles. It was assumed that at least 350 °C is required for decarboxylation to occur from the structures. The carbon dioxide loss from the samples leads us to believe that, during the course of the thermal conversion reaction, the hydroxy—imides undergo rearrangement to form a carboxy-containing benzoxazole intermediate. This carboxy—benzoxazole intermediate subsequently decarboxylates at 350 °C or higher to give the final benzoxazole product. The proposed reaction sequence is shown in Figure 19.

It is interesting to note that when the thermal conversion of **1** is attempted in the liquid or vapor phase below 350 °C (ca. 300 °C), no reaction occurs and only starting material is recovered. In fact, a carboxy—benzoxazole intermediate has not been observed or isolated from any of the model compound or polymer thermal conversion reactions.

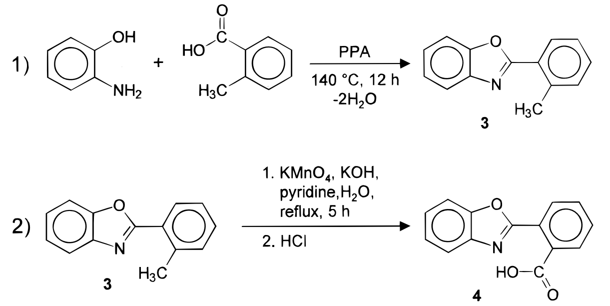

Figure 20. Synthesis of 2-(2-carboxyphenyl)benzoxazole (**4**).

To further investigate whether a carboxy—benzoxazole intermediate is involved in the thermal conversion process, 2-(2-carboxyphenyl)benzoxazole (**4**) was synthesized as shown in Figure 20. Reaction of *o*-toluic acid with 2-aminophenol in polyphosphoric acid (PPA) at 140 °C gave 2-(2-methylphenyl)benzoxazole (**3**) as white crystals in 79% yield after purification. Oxidation of the aryl methyl group of **3** with basic $KMnO_4$ resulted in the formation of **4** in 57% yield. The aryl methyl group of **3** proved to be relatively resistant to oxidation by basic potassium permanganate under various reaction conditions as evidenced by the recovery of some unreacted **3** in all cases. Attempted oxidation of **3** with CrO_3/H_2SO_4 was completely ineffective.

The liquid-phase thermal conversion of **4** was conducted at 300 and 400 °C under nitrogen using the same procedure as described for **1**. When the conversion of **4** was run at 400 °C, the same products were obtained that were observed with the conversion of **1** at 400 °C (i.e., phthalic anhydride (**9**), 2-phenylbenzoxazole (**10**), 2,2-*o*-phenylenebisbenzoxazole (**11**), carbon dioxide, water, and, most notably, *N*-(2-hydroxyphenyl)phthalimide (**1**)). Formation of these products suggests that **4** is indeed an intermediate in the thermal conversion reaction. The fact that **1** is produced during the reaction further supports the presence of **4** as an intermediate and indicates that a facile pathway exists for the thermal rearrangement of **4** to **1**. The thermal conversion of **4** was repeated in the liquid state at 300 °C (a temperature at which **1** does not react at all). To our surprise, the reaction again formed compounds **1**, **9**, **11**, and water. However, there was no formation of 2-phenylbenzoxazole (**10**) or carbon dioxide as was seen in the 400 °C reaction, indicating that 300 °C is not sufficient for decarboxylation of **4** to occur. The major product of the reaction at 300 °C was identified as **1**. Simply heating carboxy—benzoxazole (**4**) slightly above its melting point (223—225 °C) results in spontaneous rearrangement to **1**, implying that hydroxy—imide (**1**) is the more thermodynamically stable compound. Since **1** by itself does not react when heated at 300 °C, it is believed that an intermolecular reaction between **1** and **4** is necessary to account for additional products **9**, **11**, and water. From these results an overall reaction scheme can be proposed for the thermal conversion of hydroxy—imides to benzoxazoles as shown in Figure 21. It appears to be necessary to heat hydroxy—imide (**1**) to at least 350 °C in order to promote rearrangement to carboxy—benzoxazole (**4**). At this temperature, either **4** can immediately undergo intramolecular decarboxylation to give **10** and CO_2 or **4** can undergo intermolecular reaction with **1** to give additional products **9**,

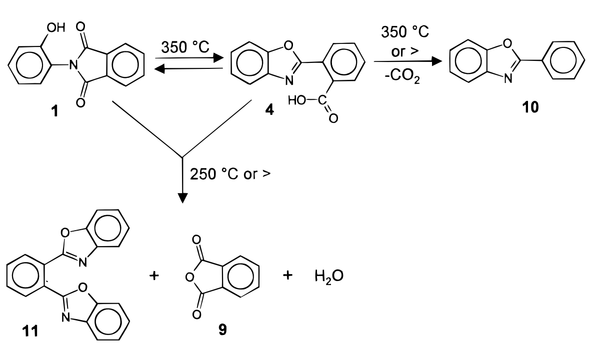

Figure 21. Overall reaction scheme for thermal conversion of hydroxy-containing imides to benzoxazoles.

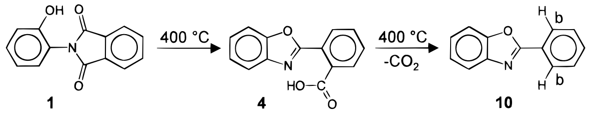

Figure 22. Expected sites of proton transfer from **1** to **10** upon thermal rearrangement of **1** to **4** followed by thermal decarboxylation of **4**.

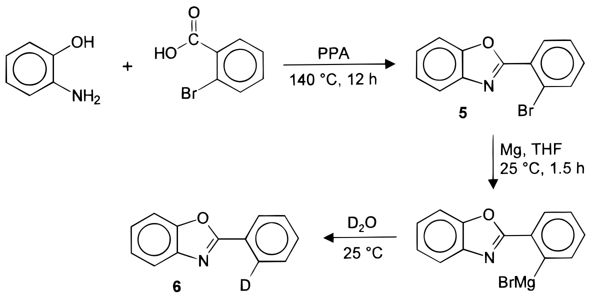

Figure 23. Synthesis of 2-(2-deuteriohydroxyphenyl)benzoxazole (**6**).

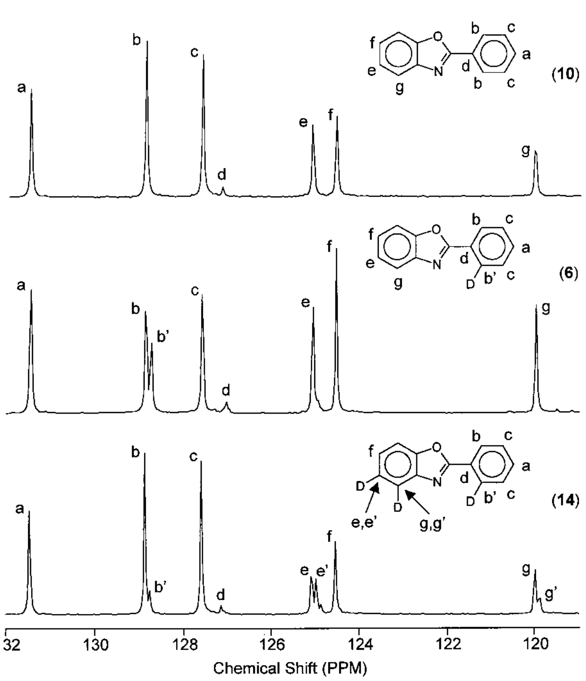

Figure 24. ^{13}C solution NMR spectra (in $CDCl_3$ with TMS) of nondeuterated 2-phenylbenzoxazole (**10**, upper trace), synthesized 2-(2-deuteriophenyl)benzoxazole (**6**, middle trace), and deuterium-containing 2-phenylbenzoxazole (**14**, lower trace) resulting from the thermal conversion of **2** at 400 °C.

11, and water. Since **4** rearranges to **1** at temperatures below 350 °C and decarboxylates at or above 350 °C, **4** is never observed or isolated from the thermal conversion reactions.

Deuterium-labeling experiments were conducted in an effort to determine more details of the thermal conversion reaction pathway. If the thermal conversion of **1** involves rearrangement to **4**, then it would be expected that the hydroxyl proton of **1** would migrate to become the carboxylic acid proton of **4**. Upon subsequent thermal decarboxylation of **4**, the carboxylic acid proton should assume one of the two equivalent positions (b) on the resulting benzoxazole **10** as shown in Figure 22. To study this proposed pathway, the hydroxyl group of *N*-(2-hydroxyphenyl)phthalimide (**1**) was deuterated by refluxing **1** in acetone with D_2O. Integration of the proton NMR spectrum showed that the product, *N*-(2-deuteriohydroxyphenyl)phthalimide (**2**), was approximately 84% deuterium exchanged. Vapor-phase thermal conversion of **2** was carried out at 400 °C, as described previously for **1**, to give an 86% isolated yield of deuterium-containing 2-phenylbenzoxazole (**14**). For comparison, an authentic sample of 2-(2-deuteriophenyl)benzoxazole (**6**) was prepared as shown in Figure 23. The reaction of 2-bromobenzoic acid with 2-aminophenol in poly(phosphoric acid) at 140 °C gave yellow crystals of 2-(2-bromophenyl)benzoxazole (**5**) in 85% yield after sublimation of the crude product. Formation of the magnesium Grignard reagent of **5** in THF followed by hydrolysis with D_2O afforded, after workup, tan crystals of **6** in 73% yield. The ^{13}C solution NMR spectra of the 2-phenylbenzoxazoles (**10**, **6**, and **14**) are compared in Figure 24. The spectrum of deuterium-labeled 2-phenylbenzoxazole (**6**), middle trace, displays an extra carbon resonance at 128.7 ppm (b′) that is not seen in nondeuterated 2-phenylbenzoxazole (**10**), upper trace. This extra resonance, due to the presence of deuterium at the b′ position, is located 0.1 ppm upfield of the normal resonance observed at carbon b for nondeuterated 2-phenylbenzoxazole (**10**) at 128.8 ppm. No splitting of the aromatic deuterium-labeled signal was observed as is seen in aliphatic compounds such as deuteriochloroform. No other extra peaks were observed in the NMR spectrum of **6**, indicating that deuterium labeling was exclusively at the b′ position. Thermal conversion of the deuterium-labeled hydroxy—imide (**2**) at 400 °C gave 2-phenylbenzoxazole (**14**), the spectrum of which is shown as the lower trace in Figure 24. The small signal at 128.7 ppm (b′, lower trace) indicates that some of the deuterium on this thermally converted benzoxazole occupies the predicted position of proton transfer shown in Figure 22. However, additional resonances for **14** (e′ and g′) are observed which are shifted 0.1 ppm upfield from the nondeutrerated carbon resonances (e and g), indicating that deuterium occupies multiple positions on the thermally converted benzoxazole. Most likely, H—D exchange reactions are occurring at the elevated temperatures (>350 °C) required for the thermal rearrangement and subsequent deuterodecarboxylation of **2**. In this case, the hydroxy—imide or carboxy—benzoxazole intermediate is believed to be the species undergoing exchange at elevated tempertures since subjecting benzoxazole (**6**) to vapor-phase thermal conversion conditions at 500 °C resulted in no change in the ^{13}C NMR spectrum of recovered **6**. Unfortunately, the resulting scrambling of the deuterium during thermal conversion makes it difficult to postulate a straightforward mechanism for the reaction. H—D exchange reactions, resulting in scrambling of the deuterium label, have previously been observed in the deuterodecarboxylation of pyridinecarboxylic acids.[21]

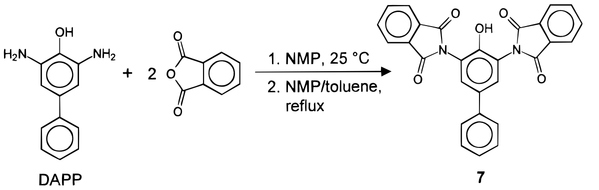

Figure 25. Two-step synthesis of hydroxy−imide model compound **7**.

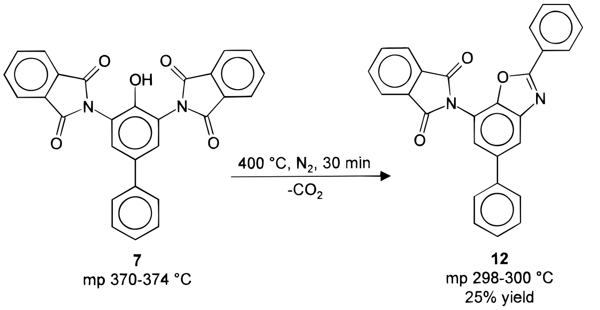

Figure 26. Thermal conversion of **7** for 30 min at 400 °C under nitrogen flow (40 mL/min) to give imide−benzoxazole **12**.

The next model compound studied was prepared by reacting phthalic anhydride with DAPP under polyimide-forming reaction conditions to give the bisphthalimide of DAPP (**7**) as shown in Figure 25. Model compound **7** was obtained as a white solid in 68% yield after recrystallization and drying (mp 370−374 °C). This model compound was synthesized in order to simulate the backbone of DAPP-containing polyimides in that there are two imide heterocycles per hydroxyl group.

Thermal conversion of **7** was performed by heating the sample (approximately 0.1 g contained in a glass boat) in a horizontal glass tube placed in a homemade temperature-controlled tube furnace. A nitrogen flow of 40 mL/min was passed through the reaction tube. In most cases, the reaction products sublimed to the cool end of the tube where they were collected and purified by recrystallization. Compound **7** was heated in the tube furnace for 30 min at 400 °C. Gas evolution was observed immediately upon melting the sample at 370 °C and slowly decreased as a yellow, crystalline product collected in the cool portion of the tube. The product, obtained in 25% yield after recrystallization from DMAc, was identified as imide−benzoxazole (**12**) (Figure 26). The IR spectra of **7** (upper trace) and **12** (lower trace) are compared in Figure 27. Before thermolysis of **7**, peaks were observed for a hydroxyl stretch centered at 3488 cm^{-1}, a strong C═O stretch at 1721 cm^{-1}, and a hydrogen-bonded C═O stretch at 1700 cm^{-1}. The hydroxyl and hydrogen-bonded C═O peaks completely disappeared upon thermolysis, indicating loss of the phenolic OH. This implied that thermolysis led to formation of imide−benzoxazole (**12**). This was confirmed by NMR. The ^1H NMR spectra of **7** and **12** are compared in Figure 28. A single proton resonance for the phenol of **7** appears at 10.3 ppm (a) in the upper trace. The phenolic proton resonance is no longer observed in the NMR spectrum of thermal conversion product **12**, lower trace, indicating that the phenol is no longer present. The ^{13}C NMR spectra of **7** and the thermal conversion product **12** are compared in Figure 29. A carbon resonance for the imide carbonyls of **7** appears at 167 ppm (a) in the upper trace. After thermal conversion, the spectrum of **12** displayed a peak characteristic of the quaternary 2-position carbon of an aromatic benzoxazole at 163 ppm (b). A carbonyl peak, shifted upfield to 166 ppm (a), is also evident in the spectrum of **12**, indicating that one of the imide rings of the model compound remained intact. Elemental analysis results were also consistent with the structure **12**.

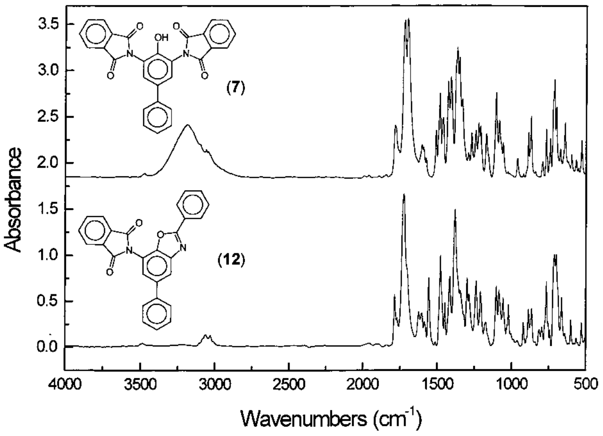

Figure 27. Comparison of the infrared spectra of **7** (upper trace) and thermal conversion product **12** (lower trace).

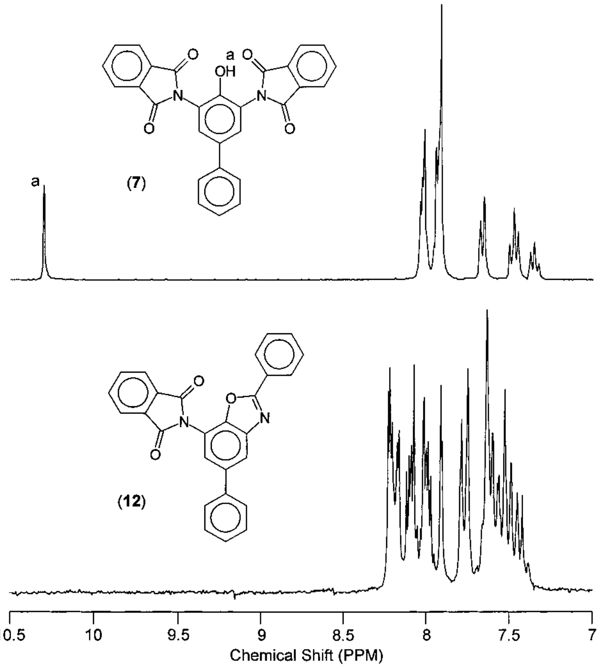

Figure 28. ^1H solution NMR spectra (in DMSO-d_6 with TMS) of hydroxy−imide model compound **7** (upper trace) and imide−benzoxazole thermal conversion product **12** (lower trace).

A hydroxy−imide model compound (**8**) with a structure similar to the BPDA−HAB polyimide was synthesized by the reaction of phthalic anhydride with HAB under reaction conditions used for the synthesis of **1**. The synthesis of bis(hydroxy−imide) **8** is shown in Figure 30. Light-brown crystals of **8** were obtained in 69% yield after recrystallization from DMAc (mp 380−384 °C).

Thermal conversion of **8** for 30 min at 400 °C under nitrogen led to the formation of the expected intramolecular reaction product, bisbenzoxazole (**13**), in approximately 5% yield after recrystallization from DMAc. The thermal conversion reaction of **8** to **13** is depicted in Figure 31. A significant amount of a black, insoluble,

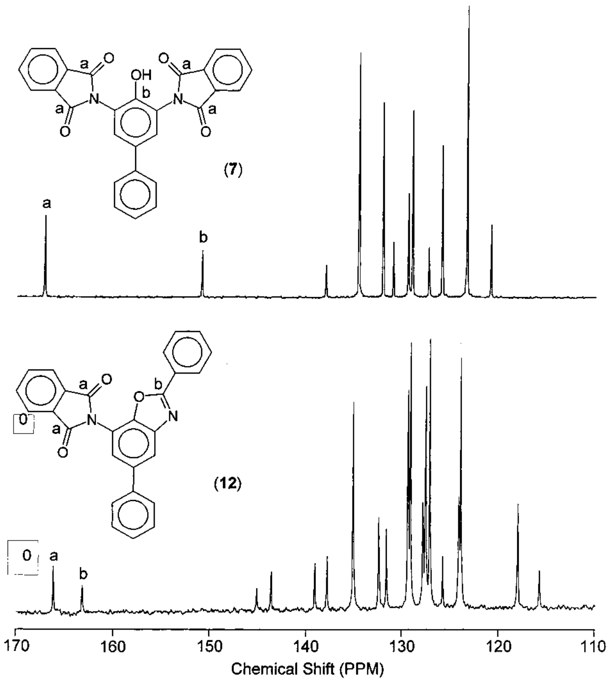

Figure 29. ^{13}C solution NMR spectra (in DMSO-d_6 with TMS) of hydroxy–imide model compound **7** (upper trace) and imide–benzoxazole thermal conversion product **12** (lower trace).

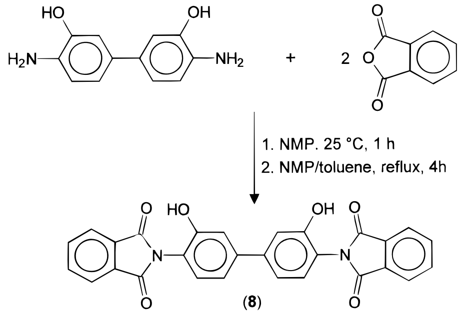

Figure 30. Two-step synthesis of bis(hydroxy–imide) model compound **8**.

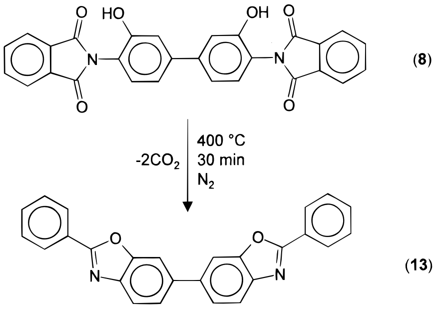

Figure 31. Thermal conversion of **8** for 30 min at 400 °C under nitrogen flow (40 mL/min) to give bisbenzoxazole **13**.

glassy residue remained in the heated portion of the tube furnace presumably formed by additional, competitive intermolecular reactions. Repeating the thermolysis of **13** in the presence of 5 mol % cuprous iodide led to the formation of **13** in 22% yield. It is believed that cuprous iodide aids decarboxlylation of the carboxy–benzoxazole intermediate, thus promoting the intramolecular reaction to form **13** and hindering intermolecular reactions such as transamidation which could lead to a cross-linked material. Copper salts are known to promote decarboxylation.[22] The low yields of **13**, with or without added copper salt, do not reflect the efficiency seen in the polyimide thermal conversion reactions where characterization results indicated that complete conversion to the polybenzoxazole occurred. The low molecular mobility of the polymer chains is believed to be responsible for the high conversions observed for the polymers due to promotion of purely intramolecular reactions. The high mobility of the molten model compounds seems to favor intermolecular reactions which leads to low yields of small molecule benzoxazoles.

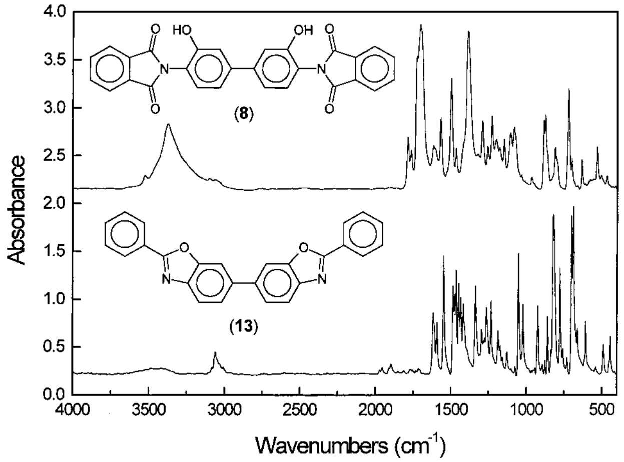

Figure 32. Comparison of the infrared spectra of **8** (upper trace) and thermal conversion product **13** (lower trace).

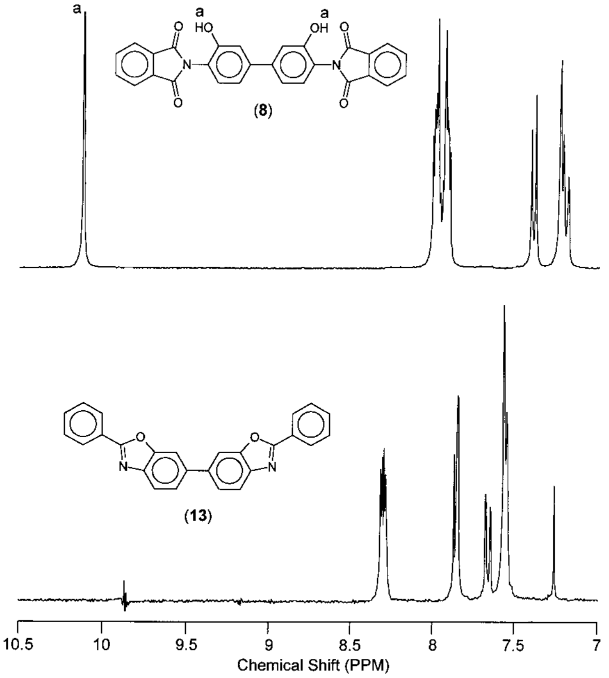

Figure 33. ^{1}H solution NMR spectra (in DMSO-d_6 with TMS) of bis(hydroxy–imide) model compound **8** (upper trace) and bisbenzoxazole thermal conversion product **13** (lower trace).

The IR spectra of **8** and **13** are compared in Figure 32. The hydroxyl stretch at 3374 cm^{-1} and C=O stretch at 1703 cm^{-1} for **8** completely disappeared upon thermal conversion. The resulting bisbenzoxazole **13** shows characteristic benzoxazole ring absorbances at 1620 and 1050 cm^{-1}. Benzoxazole formation is also supported by the NMR results. The ^{1}H NMR solution spectra of **8** and **13** are shown in Figure 33. The phenolic hydroxyl resonance (a) of **8** (upper trace) appears at 10.1 ppm downfield of TMS. The proton spectrum of **13** (lower trace) is void of hydroxyl resonances, supporting ben-

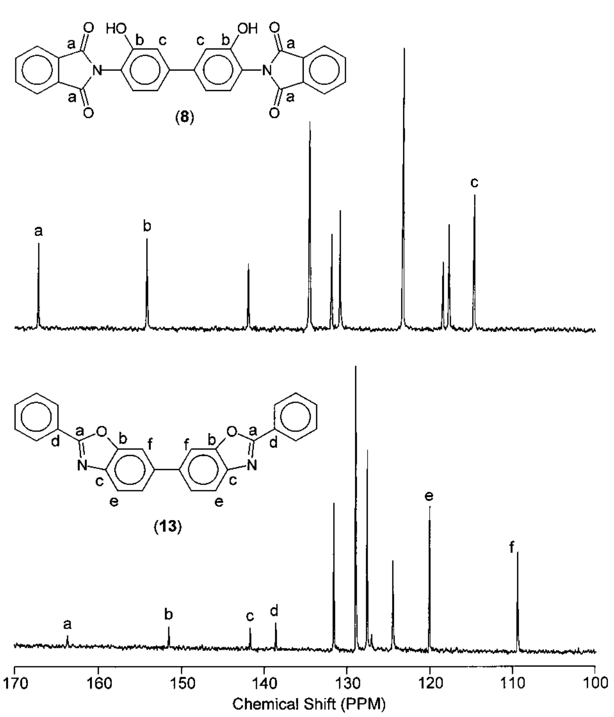

Figure 34. ^{13}C solution NMR spectra of bis(hydroxy−imide) model compound **8** (upper trace, in DMSO-d_6 with TMS) and bisbenzoxazole thermal conversion product **13** (lower trace, in $CDCl_3$ with TMS).

zoxazole formation. This particular bisbenzoxazole is highly fluorescent under 254 nm UV light.

The ^{13}C NMR spectra of **8** and **13** are compared in Figure 34. The spectrum of **13** (lower trace) shows single resonances at 109.4 (f) and 120.1 ppm (e) typical of the aromatic ring carbons ortho to the benzoxazole C−O and C−N bonds, respectively. The single characteristic peak at 163.7 ppm (a) represents the quaternary 2-position carbons of the benzoxazole rings, further supporting bisbenzoxazole formation. Elemental analysis results also support benzoxazole formation.

Conclusions

Aromatic polyimides containing hydroxyl groups ortho to the imide nitrogens were found to thermally convert to polybenzoxazoles upon heating above 350 °C in an inert atmosphere or under vacuum. The polyimide thermal conversions were accompanied by quantitative loss of carbon dioxide, indicating that an intramolecular reaction is occurring, most likely enhanced by the lower molecular mobility of the polymers. Of the 10 polyimides subjected to thermal conversions above 350 °C, only the APA-containing polyimides failed to give polybenzoxazoles, indicating that this linkage is inherently thermally unstable. The polybenzoxazoles formed by the thermolysis reaction were insoluble in all solvents tested including concentrated sulfuric acid, suggesting that some degree of cross-linking has occurred. Thermal conversion of a hydroxy−imide model compounds in the liquid state at 400 °C resulted in the formation of benzoxazoles in low yields (5−25%). The low yield of benzoxazoles from the liquid-phase thermal conversions of model compounds is believed due to predominance of intermolecular reactions occurring in the molten state where molecular mobility is much higher as compared to the polymer. Although the polyimides appeared to undergo complete conversion to polybenzoxazoles, a small amount of intermolecular reaction may be a source of cross-linking, thus giving insoluble polybenzoxazoles. Themal conversion of *N*-(2-hydroxyphenyl)-phthalimide in the vapor phase resulted in the formation of pure 2-phenylbenzoxazole in 83% yield. The vapor-phase reaction, where intermolecular reactions are minimized, appears to better simulate the thermal conversion of the polyimides. The observation that 2-(2-carboxyphenyl)benzoxazole reverts back to *N*-(2-hydroxyphenyl)phthalimide at temperatures below decarboxylation (350 °C) suggests that carboxy−benzoxazoles are low-concentration intermediates in the thermal conversion reaction. Deuterium-labeling experiments, conducted on *N*-(2-hydroxyphenyl)phthalimide, showed that scrambling of the deuterium substitution on the benzoxazole occurred upon thermal conversion, making it difficult to postulate a facile mechanism for the reaction.

Acknowledgment. This work was funded in part by a grant from Air Products and Chemicals Co. Summer fellowships for Jason M. Powers and Stacy J. Jeskey were provided by the National Science Foundation through a Research Experience for Undergraduates grant.

References and Notes

(1) Young, P. R. *J. Heterocycl. Chem.* **1972**, *9*, 371.
(2) Colson, J. G.; Michel, R. H.; Paufler, R. M. *J. Polym. Sci., Part A-1* **1966**, *4*, 59.
(3) Dawans, F.; Marvel, C. S. *J. Polym. Sci., Part A* **1965**, *3*, 3549.
(4) Perry, C. J. *J. Chem. Soc., Perkin Trans. 2* **1997**, 977.
(5) Ueda, M.; Nakayama, Y. *Macromolecules* **1996**, *29*, 6427.
(6) Yu, H. S.; Yamashita, T.; Horie, K. *Macromolecules* **1996**, *29*, 1144.
(7) Abadie, M.; Izri-Zinina, I.; Sheveleva, T. S.; Kamarova, L. G.; Rusanov, A. L.; Vygodskii, Y. S.; Shevelev, S. A.; Dutov, M. D.; Vatsadze, I. A. *Polym. Sci., Ser. A* **1997**, *39* (6), 594.
(8) Lee, H.-J.; Lee, M.-H.; Han, S. G.; Kim, H.-Y.; Won, Y. H. *Polym. Mater. Sci. Eng.* **1996**, *75*, 242.
(9) Chen, T.-A.; Jen, A. K.-Y.; Cai, Y. *J. Am. Chem. Soc.* **1995**, *117*, 7295.
(10) Tullos, G. L.; Mathias, L. J. *Polym. Commun.*, in press.
(11) So, Y. H.; Heeschen, J. P. *J. Org. Chem.* **1997**, *62*, 3552.
(12) Wolfe, J. *Concise Encyclopedia of Polymer Science and Engineering*; John Wiley & Sons: New York, 1990; p 773.
(13) Cassidy, P. E. *Thermally Stable Polymers;* Marcel Dekker: New York, 1980.
(14) Jeneke, S. A.; Johnson, P. O. *Macromolecules* **1990**, *23*, 4419.
(15) Kim, S.; Pearce, E. M.; Kwei, T. K. *Polym. Adv. Technol.* **1990**, *1*, 49.
(16) Buu-Hoi, Ng. Ph.; Lavit, D.; Xuong, Ng. D. *J. Chem. Soc* **1953**, 2612.
(17) Preston, J.; Carson, J. W. *Polymer* **1993**, *34* (4), 830.
(18) Choe, E. W.; Kim, S. N. *Macromolecules* **1981**, *14*, 920.
(19) Tashiro, K.; Yoshino, J.; Kitagawa, T.; Murase, H.; Yabuki, K. *Macromolecules* **1998**, *31*, 5430.
(20) Joseph, W. D.; Mercier, R.; Prasad, A.; Marand, H.; McGrath, J. E. *Polymer* **1993**, *34* (4), 866.
(21) Zoltewicz, J. A.; Smith, C. L.; Meyer, J. D. *Tetrahedron* **1968**, *24*, 2269.
(22) March, J. *Advanced Organic Chemistry;* John Wiley & Sons: New York, 1985; p 507.

MA981579C