

Unexpected thermal conversion of hydroxy-containing polyimides to polybenzoxazoles

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Abstract

An aromatic polyimide containing pendent hydroxyl groups *ortho* to the heterocyclic imide nitrogen was found to rearrange to a polybenzoxazole, with quantitative loss of carbon dioxide, upon heating above 400°C in an inert atmosphere. A hydroxy-containing polyimide film based on 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) and 3,3'-dihydroxy-4,4'-diaminobiphenyl (HAB) was prepared and converted to a fully aromatic polybenzoxazole by heating at 500°C for 1 h under nitrogen. The resulting polybenzoxazole film was found to be amorphous by small angle X-ray scattering (SAXS). The film also displayed excellent solvent resistance and good thermal stability by thermogravimetric analysis with 5% weight loss in nitrogen occurring at 625°C. A hydroxy-containing imide model compound was also found to undergo thermal conversion to a bisbenzoxazole when heated above 400°C under nitrogen. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Soluble hydroxy-containing polyimides have recently been studied as potential high glass transition temperature (T_g), thermally stable polymers for photoresist [1–3] and non-linear optical (NLO) applications [4]. The pendent hydroxyl group on the fully imidized polymer is available for post-polymerization reactions such as NLO chromophore attachment under mild reaction conditions [5]. We became interested in potential use of hydroxy-containing polyimides for incorporation of other useful functionality. During the process of characterizing these materials, we discovered an unexpected thermogravimetric analysis (t.g.a.) weight loss (corresponding to one CO₂ per imide) that implied in situ thermal conversion of the hydroxy-containing polyimide to an aromatic polybenzoxazole. We describe here confirmation of this novel rearrangement process.

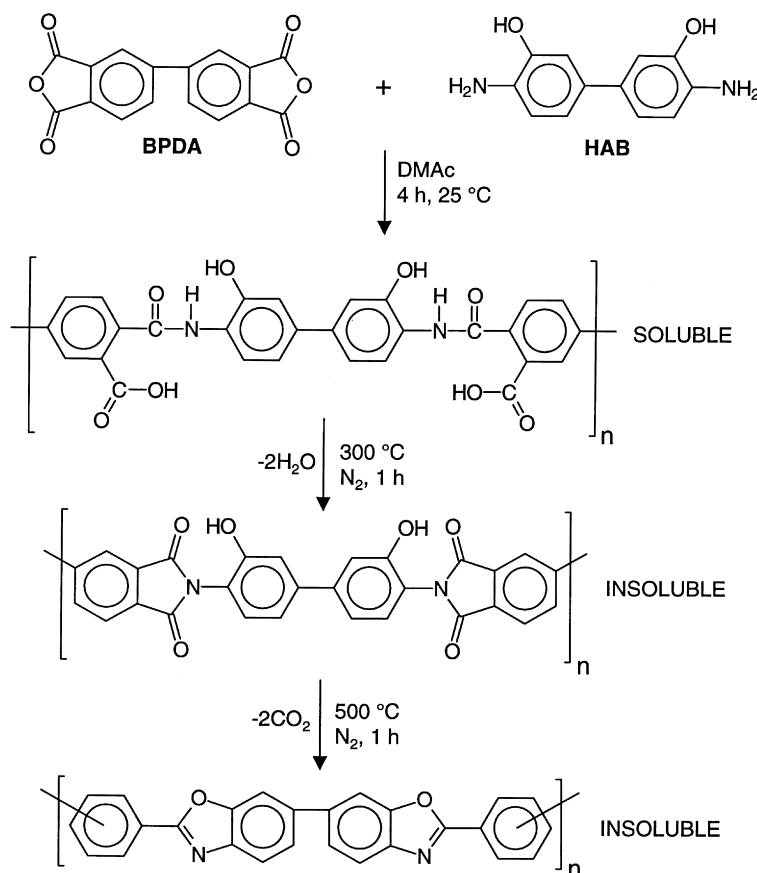
Aromatic polybenzoxazoles (PBOs) display excellent thermal stability plus good solvent and chemical resistance [6]. The properties of aromatic polybenzoxazoles that make them attractive for many applications also leads to difficulties in synthesis and fabrication. Wholly aromatic PBOs, in

fact, are soluble only in strong acids (e.g., sulfuric, methane sulfonic, triflic, and polyphosphoric acids) [7,8] and more recently through complex-mediated solubilization in Lewis acid/solvent systems such as AlCl₃/nitromethane [9]. In situ thermal conversion of hydroxy-containing polyimides to polybenzoxazoles could provide an alternative method for generating polybenzoxazole films, fibres and composites that are difficult to obtain otherwise.

2. Methods and materials

BPDA and HAB were obtained from Chriskev Company. HAB was purified by recrystallization from *N,N*-dimethylformamide (DMF)/ethanol mixture. BPDA was used as received. All other reagents and solvents were used as received. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ. Intrinsic viscosity measurement was obtained in DMAc solution at 30°C using an Ubbelohde viscometer. Infrared spectra were recorded on an ATI-Mattson Galaxy 5020 spectrometer. Solution ¹H and ¹³C n.m.r. were obtained on a Bruker AC-300 instrument using standard acquisition parameters. Solid-state ¹³C n.m.r. spectra were acquired 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

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Scheme 1. Synthesis of BPDA–HAB polyamic acid and thermal conversion to hydroxy-containing polyimide and polybenzoxazole.

proton decoupling with sample spinning rates > 4.0 kHz. D.s.c. and t.g.a. analyses were conducted on TA instruments 2920 and 2060 modules, respectively, controlled by a Thermal Analyst 2100.

HAB (3.000 g, 10.197 mmol) and DMAc (10 ml) were added to a dry, nitrogen-purged flask at ambient temperature. After mechanical stirring to give a light-brown solution, BPDA (3.000 g, 10.197 mmol) and DMAc (10 ml) were added to bring the solids content to 20% (w/v), resulting in a slight exotherm. The yellow reaction mixture was stirred for 2 h to give a highly viscous solution that was diluted with DMAc (25 ml) so that stirring could be continued for an additional 2 h. Thermal solution imidization, using toluene/water azeotrope, was conducted on half of the polyamic acid. Polymer precipitation occurred before complete imidization. The remaining half of the BPDA–HAB polyamic acid solution was diluted with DMAc (50 ml) and used to obtain viscosity measurement and cast thin films onto glass microscope slides. The intrinsic viscosity of the polyamic acid was 0.82 dl/g in DMAc at 30 °C.

The films of the polyamic acid were dried under vacuum at 60 °C for 1 h and 120 °C for 2 h, then thermally cyclized to the hydroxy-containing polyimide at 300 °C for 1 h under nitrogen to give an insoluble material. T.g.a. 5% weight loss in N₂ occurred at 422 °C with 18.6% weight loss from 325–600 °C in nitrogen; no T_g was observed by

d.s.c.; polyimide ¹³C CP/MAS δ 167.5, 152.6, 142.6, 132.0, 118.9; i.r. (thin-film) 3385 (OH), 1775, 1714 (C=O), 1380 cm⁻¹; Anal. calcd for C₂₈H₁₄N₂O₆: C, 70.89; H, 2.97; N, 5.90%; Found: C, 70.64; H, 3.18; N, 5.94%.

While still adhered to glass slides, the yellow BPDA–HAB polyimide films were heated at 500 °C for 1 h under nitrogen to give purple–brown, insoluble polybenzoxazole films which were released from the glass by immersion in water. T.g.a. 5% weight loss in nitrogen occurred at 625 °C; no T_g or T_m was observed by d.s.c. up to 500 °C; ¹³C CP/MAS δ 163.2, 151.6, 141.4, 127.1, 108.5; i.r. (thin-film) 3040 (Ar C–H), 1617, 1485, 1461, 1266, 1058, 828, 813 cm⁻¹; Anal. calcd for C₂₆H₁₄N₂O₂: C, 80.82; H, 3.65; N, 7.25%; Found: C, 80.46; H, 3.76; N, 7.00%.

HAB (5.00 g, 23.1 mmol), phthalic anhydride (6.85 g, 46.2 mmol), DMAc (40 ml) and toluene (10 ml) were placed in a 100 ml round bottom flask fitted with a Dean-Stark trap, reflux condenser, stir bar and nitrogen purge. The reaction mixture was stirred at ambient temperature for 1 h. A small exotherm was observed initially during formation of the amic acid. The reaction was refluxed for 4 h to remove the water of imidization as the toluene/water azeotrope. Excess toluene was removed by distillation and after cooling, the flask contents were poured into 200 ml of a stirring methanol/water mixture (1:1 by volume). The

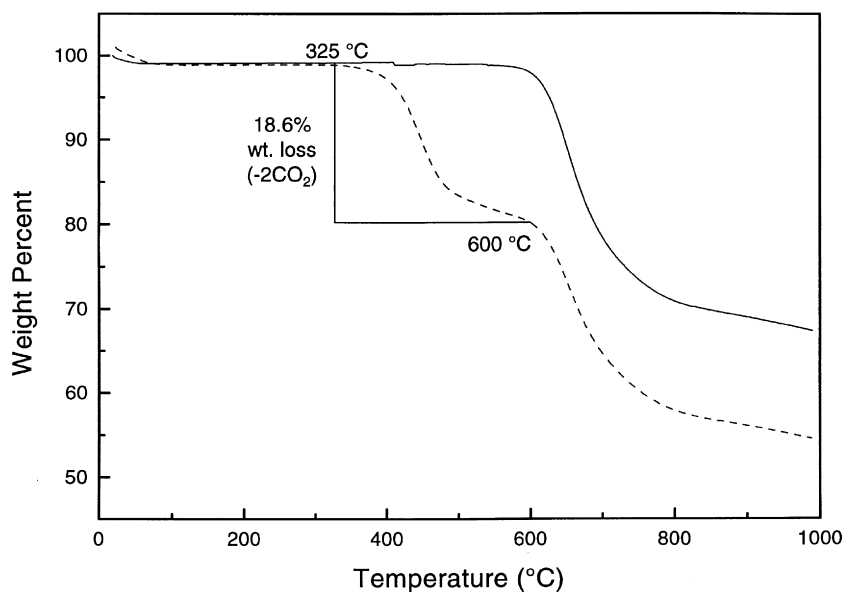


Fig. 1. T.g.a. in nitrogen of BPDA–HAB polyamic acid after heating 1 h at 300° in nitrogen (dashed line) and 1 h at 500°C in nitrogen (solid line).

resulting 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; ^1H n.m.r. (DMSO- d_6 with TMS): δ 10.12 (s, OH), 7.99 (m), 7.93 (m), 7.40 (d), 7.21 (m); ^{13}C n.m.r. (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; i.r. (KBr) 3374 (O–H), 1785, 1725, 1703 (C=O), 1497, 1385, 719 (cm^{-1}); Anal. calcd for $\text{C}_{28}\text{H}_{16}\text{N}_2\text{O}_6$: C, 70.59; H, 3.38; N, 5.88%; Found: C, 70.51; H, 3.70; N, 5.67%.

A glass tube (5 mm I.D. \times 7 mm O.D. \times 180 mm) open on both ends was charged at one end with BPHAB (0.1112 g, 0.2334 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. Tube temperature was monitored with a thermocouple. Gas evolution was observed when the reaction mixture became molten (*ca.* 380°C). The resulting yellow crystalline solid which collected in the cold portion of the tube was removed, recrystallized from DMAc, collected by filtration, and dried in vacuo at 120°C for 4 h to give bisbenzoxazole (BB1) as white, plate-like crystals; yield 0.0039 g, 5%; mp 264–267°C; ^1H n.m.r. (CDCl_3 with TMS): δ 8.29 (m), 7.85 (m), 7.65 (t), 7.56 (t); ^{13}C n.m.r. (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; i.r. (KBr) 3059, 1619, 1548, 1052, 821, 701, 689 (cm^{-1}); Anal. calcd for $\text{C}_{26}\text{H}_{16}\text{N}_2\text{O}_2$: C, 80.40; H, 4.15; N, 7.21%; Found: C, 80.43; H, 4.25; N, 6.97%. Repeating the thermal rearrangement of BPHAB in the presence of copper (I) iodide (5 mol %) resulted in a 22% yield of bisbenzoxazole BB1 after recrystallization and drying.

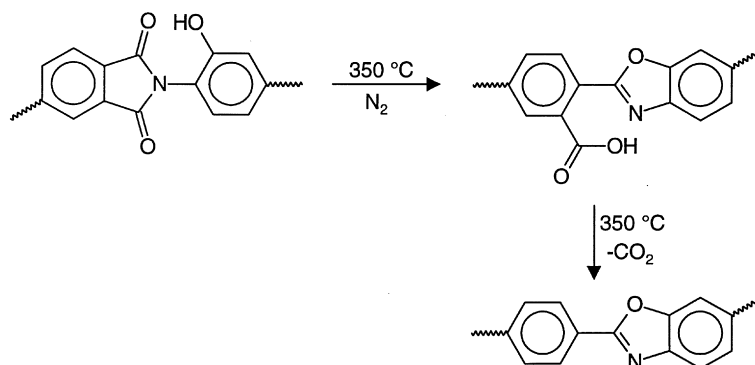
3. Results and discussion

Reaction of 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) with 3,3'-dihydroxy-4,4'-diaminobiphenyl (HAB) in *N,N*-dimethylacetamide (DMAc) at ambient temperature gave the soluble polyamic acid shown in Scheme 1. Attempted thermal solution imidization to the hydroxy-containing polyimide gave an insoluble, partially imidized product. The BPDA–HAB polyimide was finally prepared via thermal imidization of solution cast (DMAc) thin-films of the polyamic acid by heating for 1 h under nitrogen at 300°C.

During routine thermogravimetric analysis of the BPDA–HAB polyimide in nitrogen, Fig. 1, a well-defined weight loss comprising 18.6% of the sample weight was observed between 325 and 600°C. Calculations revealed that expulsion of 2 mol of carbon dioxide per repeat unit would exactly account for this weight loss. Heating of a yellow polyimide film for 1 h in the region of weight loss (*ca.* 500°C, Scheme 1) gave a purple–brown film which, when tested by t.g.a. under nitrogen, showed that the temperature for 5% weight loss increased to 625°C (solid line in Fig. 1). The inherent thermal stability of the material obtained after the 18.6 weight loss is also consistent with conversion to a polybenzoxazole above \sim 350°C.

The proposed sequence is shown in Scheme 2, where the hydroxy-imide rearranges to a carboxy-benzoxazole intermediate followed by decarboxylation above 350°C to give the final, fully aromatic benzoxazole product.

Thermal conversion of the hydroxy-containing polyimide to polybenzoxazole was monitored by FT-i.r. Thin-film samples of BPDA–HAB polyamic acid were heated under nitrogen atmosphere for 1 h at 120, 225, 300, 400 and 500°C. The i.r. spectra of these samples are shown in Fig. 2. Cyclization of the BPDA–HAB polyamic acid to



Scheme 2. Proposed reaction for thermal conversion of hydroxy-imide to benzoxazole.

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 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 ¹³C n.m.r. spectra were obtained on samples of BPDA-HAB polyamic acid that had been heated for 1 h each at 300 and 500°C (Fig. 3). A peak for imide carbonyls at 167 ppm (a) is present in the upper trace of the hydroxy-containing polyimide formed by heating 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 of the benzoxazole ring. Microanalysis results confirmed the chemical compositions of the polyimide and polybenzoxazole. Finally, results of small angle X-ray scattering (SAXS) indicate a completely amorphous structure for the BPDA-HAB-derived aromatic polybenzoxazole in contrast to highly crystalline all-*para* all-aromatic PBO [10]. 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 polybenzoxazole copolymers based on 2,2-bis(3-amino-4-hydroxyphenyl)propane and iso- and terephthaloyl chlorides. Crystallinity decreased dramatically as the incorporation of *meta*-oriented isophthaloyl species increased [11].

We have investigated this thermolysis reaction on a hydroxy-containing imide model compound (BPHAB) derived from HAB and phthalic anhydride.

The synthesis and thermal conversion of BPHAB to

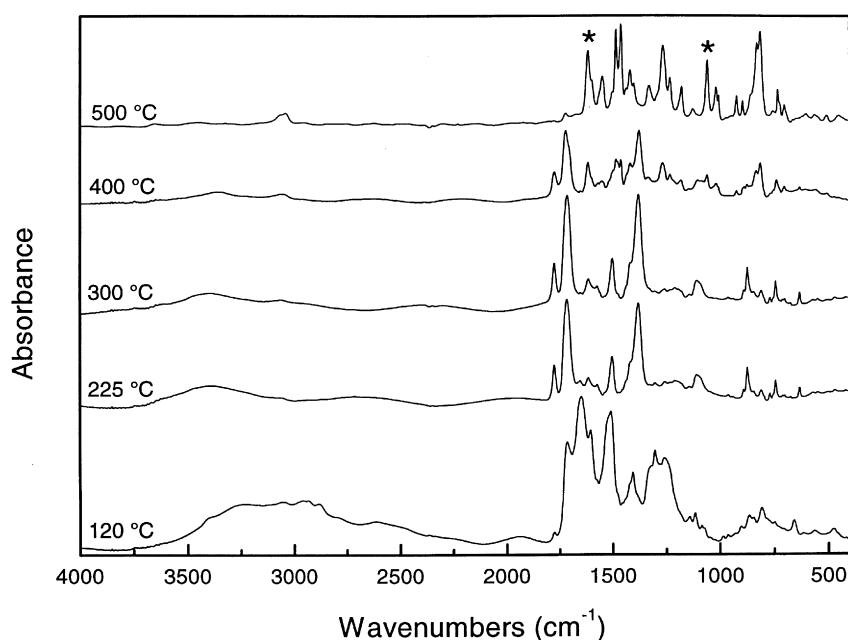
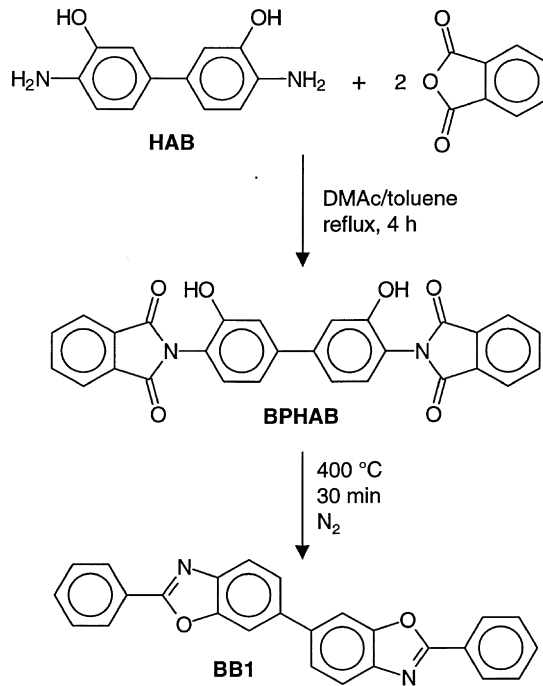


Fig. 2. FT-i.r. spectra (thin films) of BPDA-HAB polyamic acid after heating 1 h at indicated temperatures.



Scheme 3. Synthesis of hydroxy-containing imide model compound (BPHAB) and thermal conversion to bisbenzoxazole (BB1).

bisbenzoxazole (BB1) is shown in Scheme 3. Reaction of HAB with 2 mol of phthalic anhydride in DMAC/toluene gave BPHAB in 69% yield. Heating BPHAB to 400°C in a horizontally suspended glass tube under nitrogen flow (40 ml/min) resulted in the formation and sublimation of BB1 to the cool portion of the tube. Upon recrystallization

of the sublimed material from DMAC, pure BB1 was obtained in 5% yield. Repeating the thermal conversion reaction of BPHAB in the presence of copper (I) iodide (5 mol.%) resulted in the formation of 22% pure BB1 after recrystallization. It is believed that the yield of BB1 is low due to intermolecular reactions that occur to give an

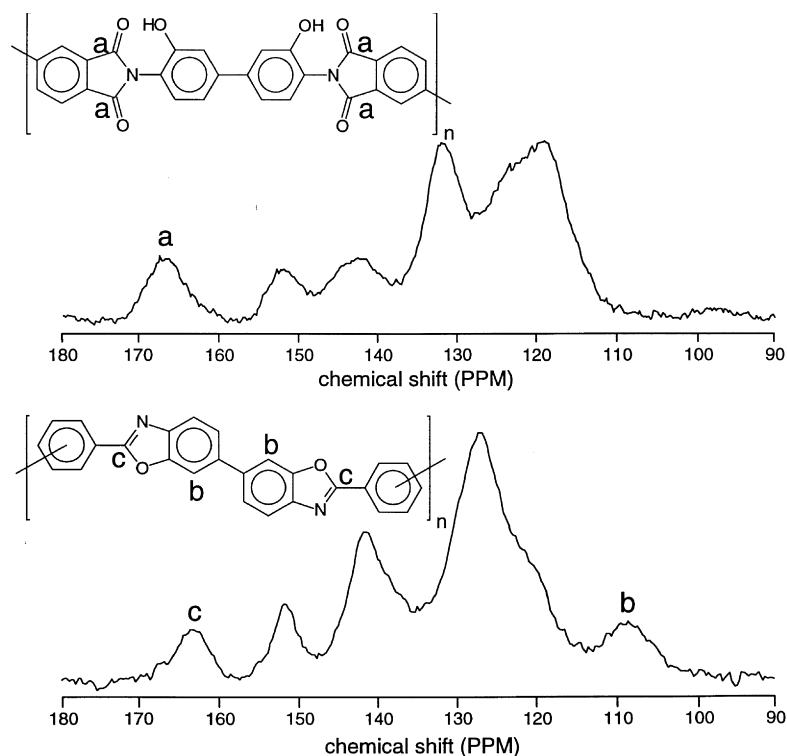


Fig. 3. Solid-state ¹³C CP/MAS n.m.r. of BPDA–HAB polyimide (upper trace) and polybenzoxazole thermolysis product (lower trace).

insoluble residue in the heated portion of the glass tube. The addition of cuprous iodide appears to enhance decarboxylation while suppressing possible intermolecular reactions, thus giving a higher yield of BB1. The yield of BB1 is quite low compared to the results obtained during thermolysis of the BPDA–HAB polyimide. T.g.a. analysis indicates quantitative carbon dioxide loss during thermal conversion of the polyimide. Elemental analysis, solid-state n.m.r. and infrared spectroscopy support exclusive polybenzoxazole formation. This seems to indicate that low molecular motion in the polymer favours intramolecular reaction (benzoxazole formation), whereas intermolecular reactions become significant during thermolysis of the model compound in the molten state. The formation of benzoxazoles from the hydroxy-containing imide model compound and polyimide supports the generality of this reaction. The thermal conversion reaction is currently being extended to other model compounds and polymers.

4. Conclusions

An aromatic polyimide containing hydroxyl groups *ortho* to the imide nitrogens was found to rearrange to a polybenzoxazole upon heating above 400°C in an inert atmosphere. The thermal rearrangement was accompanied by quantitative loss of carbon dioxide, indicating an intramolecular reaction possibly enhanced by the lower molecular mobility of this high T_g material. Thermal conversion of a hydroxy-containing bisimide model compound at 400°C resulted in the formation of a bisbenzoxazole, albeit in low yield, further confirming generality of the reaction. The low

yield of bisbenzoxazole from the model compound is believed due to predominance of intermolecular reactions occurring in the molten state where molecular mobility is much higher as compared to the polymer. The polybenzoxazole obtained upon thermal conversion of the BPDA–HAB polyimide at 500°C displayed excellent solvent resistance and thermal stability and was found to be amorphous by SAXS.

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