Synthesis of polybenzimidazoles via aromatic nucleophilic substitution reactions of self-polymerizable (A-B) monomers*

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Self-polymerizable (A-B) polybenzimidazole (PBI) monomers have been prepared and converted to PBIs via aromatic nucleophilic substitution reactions. Thus, 2(4-fluorophenyl)-5(6)-hydroxy-benzimidazole (FHB) and 2-(4-fluorophenyl)-5-hydroxy-1-phenylbenzimidazole (PFHB) have been prepared and polymerized at 230°C to 250°C in *N*-cyclohexyl-2-pyrrolidinone (CHP) containing potassium carbonate. The imidazole ring in these monomers activated the fluorine atom for nucleophilic displacement by the phenate ion. The resulting polymers were soluble in *N*-methyl-2-pyrrolidinone (NMP) and had intrinsic viscosities that ranged from 0.6 to 2.6 dl g^{-1} (NMP at 30°C). The PBI obtained from FHB was semicrystalline with a glass transition temperature (T_g) of 365°C, while the poly(*N*-phenylbenzimidazole) (PPBI) obtained from PFHB was amorphous with a T_g of 278°C. Thin films of the PPBI polymer were tough and flexible, having tensile strengths as high as 100 MPa, while those of the PBI polymer were brittle. The PBI retained 95% of its weight to 460°C when subjected to thermogravimetric analysis (t.g.a.) in air, while the PPBI retained 95% of its weight to 535°C under the same conditions. In order to lower the T_g and also to improve the mechanical properties of the PBI, PFHB was copolymerized with FHB. The T_g values of the copolymers decreased from 342°C to 296°C as their PFHB content increased from 25 to 75 mol%, while the tensile strengths of thin films of the copolymers increased with increasing PFHB content. Random copolymers were also prepared from a self-polymerizable poly(phenylquinoxaline) (PPQ) monomer and FHB.

(Keywords: self-polymerizable polybenzimidazole monomers; aromatic nucleophilic substitution; polybenzimidazole; poly(*N*-phenylbenzimidazole); semicrystalline; amorphous; thin films; thermally stable; benzimidazole copolymers; poly(phenylquinoxaline))

INTRODUCTION

Polybenzimidazoles (PBIs) are a class of high temperature/high performance polymers that have been commercialized[1]. PBIs are generally obtained from the condensation reactions of aromatic bis(*o*-phenylenediamines) with aromatic dicarboxylic acid derivatives. However, the reactions must be carried out at very high temperatures or in acid solvents such as polyphosphoric acid (PPA). The aromatic bis(*o*-phenylenediamines) are also expensive and difficult to purify. Therefore, there is considerable incentive to develop alternative synthetic routes to these materials.

Recently, aromatic nucleophilic substitution reactions have been used to prepare heterocyclic polymers, the latter having previously been prepared using conventional condensation reactions[2–6]. One part of this approach has been to use the electron-withdrawing heterocyclic ring to activate a leaving group for nucleophilic substitution. For example, poly(phenylquinoxaline) (PPQ) self-polymerizable (A-B) monomers, i.e. 6-fluoro-2-(4-hydroxyphenyl)-3-phenylquinoxaline and 6-fluoro-3-(4-hydroxyphenyl)-2-phenylquinoxaline, have been prepared and polymerized in this laboratory[7–9]. In these monomers the pyrazine ring activates the fluorine atom for nucleophilic displacement by the phenate ion.

During the course of this work, Smith Jr *et al.*[10] prepared PBIs using aromatic nucleophilic substitution reactions. In their work they synthesized bisphenol monomers that contained the benzimidazole moiety, which were then polymerized with activated aromatic difluorides. In this research it was postulated that an imidazole ring could also activate leaving groups. In fact, the objective in this case was the synthesis and polymerization of A-B PBI monomers that contained both a phenol moiety and a site activated for nucleophilic substitution by an imidazole ring. The A-B-monomer approach was chosen to further simplify the route to the desired PBIs. Vogel and Marvel[11] and Kovar and Arnold[12] had previously used a similar approach with conventional PBI chemistry. Both groups prepared and polymerized A-B monomers containing *o*-phenylenediamine moieties and ester groups. A major part of the present study was to determine the optimum conditions for the polymerization of the monomers that were synthesized, and a thorough characterization of the polymers that were obtained.

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EXPERIMENTAL

Instrumentation

Infra-red spectra were obtained with a Beckman FT-2100 Fourier transform spectrophotometer, and ^1H n.m.r. spectra were obtained at 200 MHz using a Varian Gemini-200 spectrometer. ^{19}F n.m.r. spectra were obtained on a General Electric 300 nuclear magnetic resonance spectrometer, operating at 300 MHz. Elemental analyses were carried out by Galbraith Laboratories, Knoxville, TN, USA, while all of the melting points were determined on a Mel-Temp melting point apparatus and are uncorrected. Intrinsic viscosities were determined with a Cannon–Ubbelohde No. 100 viscometer, with the flow times recorded for NMP solutions, having polymer concentrations of approximately 0.5 to 0.25 g $(dl)^{-1}$, at 30 ± 0.1°C. Differential scanning calorimetry (d.s.c.) analyses were performed in nitrogen with a heating rate of 10°C min^{-1} using a DuPont Model 9900 thermal analyser equipped with a differential scanning calorimetry cell. Thermogravimetric analyses (t.g.a.) were carried out both in nitrogen and in air with a DuPont Model 951 thermogravimetric analyser, employing a heating rate of 10°C min^{-1}. Dynamic mechanical thermal analysis (d.m.t.a.) thermograms were obtained in a nitrogen atmosphere using a Polymer Laboratories thermal analyser, with a heating rate of 1°C min^{-1}.

Materials

Polyphosphate ester (PPE) was prepared from phosphorous pentoxide and diethyl ether by a previously reported procedure[13]. Copper powder was obtained from the reduction of $CuSO_4$ with Zn[14]. *m*-Cresol, *N*-cyclohexyl-2-pyrrolidinone (CHP), *N*,*N*-dimethylacetamide (DMAc), and *N*-methyl-2-pyrrolidinone (NMP) were distilled from P_2O_5 under reduced pressure immediately prior to use. Diphenylsulfone (DPS) was recrystallized from methanol, while the remainder of the reagents and solvents were purchased from commercial sources and used as received.

Monomer syntheses

Preparation of 1,2-diamino-4-methoxybenzene (**2**). A solution of 4-methoxy-2-nitroaniline (30.00 g, 0.1784 mol) in ethanol (200 ml) containing 5 wt% palladium on activated carbon (1.00 g) was placed in a hydrogenation apparatus, and the mixture was agitated under hydrogen (4.5×10^5 Pa) at room temperature for 4 h. The mixture was filtered, and the filtrate concentrated on a rotary evaporator. The residue was then distilled under reduced pressure to afford 12.90 g (53% yield) of a yellow liquid (b.p. 240–242°C at 5 mm Hg; i.r. (neat) 3499 and 3340 cm^{-1} (N–H)).

Preparation of 2-(4-fluorophenyl)-5(6)-methoxybenzimidazole (**4**). To a 500 ml, three-necked, round-bottom flask, equipped with an overhead stirrer, a condenser and a nitrogen inlet, were added compound **2** (5.00 g, 0.0362 mol) and PPE (30 g). The reaction mixture was heated at 100°C until the diamine completely dissolved, and 4-fluorobenzoic acid (5.07 g, 0.0362 mol) was then added. The reaction mixture was heated at 120°C for 1 h, allowed to cool to room temperature, and poured into water (500 ml). The precipitate that formed was collected by filtration and dried in air, and the resulting solid was extracted with diethyl ether. The diethyl-ether extract was reduced to dryness on a rotary evaporator, and the residue was sublimed to give 2.00 g (23% yield) of a white powder (m.p. 186–188°C). The ^1H n.m.r. (acetone-d^6) spectrum showed peaks at $\delta = 8.3$–7.8 (m, aromatic, 7H) and 3.8 ppm (s, OCH_3, 3H). Elemental analysis found: C, 68.79; H, 4.50; N, 11.33%. $C_{14}H_{11}FN_2O$ requires: C, 69.41; H, 4.58; N, 11.56%.

Preparation of 2-(4-fluorophenyl)-5(6)-hydroxybenzimidazole (*FHB*) (**6**). To a 250 ml, three-necked, round-bottom flask were charged compound **4** (5.00 g, 0.0206 mol), acetic acid (25 ml) and 48% hydrobromic acid (50 ml). The reaction mixture was heated at 120°C for 4 h. After cooling to room temperature, it was stored at room temperature for 24 h, after which the white needles that formed were collected by filtration and dried in air. The crude product was stirred in a 5% aqueous sodium bicarbonate solution and then recrystallized from aqueous ethanol to yield 4.10 g (87% yield) of yellow needles (m.p. 260–262°C). The ^1H n.m.r. (DMSO-d^6) spectrum showed peaks at $\delta = 9.2$ (s, OH, 1H) and 8.2–7.6 ppm (m, aromatic, 7H). Elemental analysis found: C, 67.47; H, 3.93; N, 12.34%. $C_{13}H_9FN_2O$ requires: C, 68.41; H, 3.98; N, 12.28%.

Preparation of 2-(2-fluorophenyl)-5(6)-methoxybenzimidazole. This compound was prepared from **2** and 2-fluorobenzoic acid by the procedure previously described for compound **4**. The crude reaction product was sublimed to give an 18% yield of a white powder (m.p. 186–188°C). The ^1H n.m.r. (acetone-d^6) spectrum showed peaks at $\delta = 8.3$–6.8 (m, aromatic, 7H) and 3.8 ppm (s, OCH_3, 3H).

Preparation of 2-(2-fluorophenyl)-5(6)-hydroxybenzimidazole (*7*). Monomer **7** was prepared from 2-(2-fluorophenyl)-5(6)-methoxybenzimidazole by the procedure described for compound **6**. The crude reaction product was recrystallized from aqueous ethanol to give a 92% yield of yellow needles (m.p. 275–277°C). The ^1H n.m.r. (DMSO-d^6) spectrum showed peaks at $\delta = 9.3$ (s, OH, 1H) and 8.2–7.3 ppm (m, aromatic, 7H).

Preparation of 1,2-diamino-4-fluorobenzene (**9**). A solution of 4-fluoro-2-nitroaniline (65.96 g, 0.0421 mol) in ethyl acetate (150 ml), containing 5 wt% palladium on activated carbon (0.81 g), was placed in a hydrogenation apparatus. The mixture was agitated under hydrogen (4.5×10^5 Pa) at room temperature for 4 h, after which the mixture was filtered, and the filtrate then concentrated on a rotary evaporator. The residue was sublimed under reduced pressure at 80°C to afford 48.00 g (90% yield) of a white powder, with m.p. 98–99°C (cf. m.p. of 98°C previously reported[15]).

Preparation of 5(6)-fluoro-2-(3-methoxyphenyl)benzimidazole (*11*). To a 500 ml, three-necked, round-bottom flask, equipped with an overhead stirrer, a condenser and a nitrogen inlet, were added compound **9** (5.05 g, 0.0400 mol) and PPE (40.0 g). The reaction mixture was heated at 100°C until the diamine completely dissolved, and *m*-anisic acid (5.01 g, 0.0329 mol) was then added. The reaction mixture was heated at 120°C for 1 h, allowed to cool to room temperature, and then poured into water (500 ml). The precipitate that formed was collected by filtration and dried in air. The solid was

extracted with diethyl ether. The extract was reduced to dryness on a rotary evaporator, and the residue was then sublimed to give 3.69 g (46% yield) of a white powder (m.p. 206–207°C). The ^{1}H n.m.r. (acetone-d^6) spectrum showed peaks at $\delta = 7.3$–6.5 (m, aromatic, 7H) and 3.4 ppm (s, OCH_3, 3H).

Preparation of 5(6)-fluoro-2-(3-hydroxyphenyl)benzimidazole (***12***). To a 250 ml, three-necked, round-bottom flask were added compound **11** (5.00 g, 0.0206 mol), acetic acid (25 ml) and 48% hydrobromic acid (50 ml). The reaction mixture was heated at 120°C for 4 h, and after cooling to room temperature, was then stored at room temperature for 24 h. The needles that formed were collected by filtration and dried in air. The crude reaction product was stirred in 5% aqueous sodium bicarbonate solution, and then recrystallized from aqueous ethanol to yield 3.39 g (72% yield) of white needles (m.p. 281–283°C). The ^{1}H n.m.r. (DMSO-d^6) spectrum showed peaks at $\delta = 9.3$ (s, OH, 1H) and 7.1–6.4 ppm (m, aromatic, 7H).

Preparation of 4-methoxy-2-nitrodiphenylamine (***14***). To a 500 ml, three-necked, round-bottom flask were added 4-methoxy-2-nitroaniline (50.00 g, 0.2794 mol), bromobenzene (270 ml), K_2CO_3 (21.00 g), KI (1.50 g) and freshly reduced copper (0.90 g)[14]. The reaction mixture was heated at 180°C for 16 h, and during this time, four further portions of copper (in 0.50 g quantities) were added at regular intervals. The mixture was allowed to cool to room temperature, and the solids were removed by filtration. The bromobenzene was removed from the filtrate by steam distillation, and the residue that remained was dissolved in diethyl ether and washed with 2 N HCl. The diethyl ether was removed on a rotary evaporator, and the residue was finally purified by flash column chromatography on silica gel with 10 vol% ethyl acetate/hexane mixture to afford 14.50 g (20% yield) of a red powder with m.p. of 48–49°C (cf. literature m.p. of 48°C[16]).

Preparation of 2-amino-4-methoxydiphenylamine (***15***). A solution of compound **14** (6.10 g, 0.0250 mol) in ethyl acetate (40 ml), containing palladium on activated carbon (5 wt%, 0.50 g), was placed in a hydrogenation apparatus. The mixture was agitated under hydrogen (4.5×10^5 Pa) at room temperature for 4 h, after which time the mixture was filtered and the filtrate removed on a rotary evaporator. The residue was distilled under reduced pressure to afford 2.94 g (55% yield) of a white powder, with m.p. of 98–99°C (cf. literature m.p. of 98°C[16]).

Preparation of N-(4-fluorobenzoyl) 2-amino-4-hydroxydiphenylamine (***17***). To a 100 ml, three-necked, round-bottom flask was added a solution of compound **15** (3.05 g, 0.0142 mol) in DMAc (20 ml). The reaction mixture was cooled to −5°C, and 4-fluorobenzoyl chloride (2.25 g, 0.0142 mol) was added slowly. The mixture was stirred at 0°C for 6 h and then poured into water (300 ml). The precipitate that formed was collected by filtration and recrystallized from aqueous ethanol to afford 4.40 g (92% yield) of white needles (m.p. 119–121°C). The i.r.(KBr) spectrum showed peaks at 3377 and 3296 (N–H) and 1654 cm^{-1} (C=O). Elemental analysis found: C, 71.16; H, 5.32; N, 8.39%. $C_{20}H_{17}FN_2O_2$ requires: C, 71.41; H, 5.10; N, 8.33%.

Preparation of 2-(4-fluorophenyl)-5-methoxy-1-phenylbenzimidazole (***18***). Compound **17** (3.00 g, 0.0089 mol) was heated at 260°C, under reduced pressure, for 6 h. The residue was sublimed to afford 2.36 g (83% yield) of a white powder (m.p. 140–141°C). The i.r.(KBr) spectrum showed a peak at 1600 cm^{-1} (C=N), and the ^{1}H n.m.r. (acetone-d^6) spectrum peaks at $\delta = 7.6$–6.9 (m, aromatic, 12H) and 3.85 ppm (s, OCH_3, 3H). Elemental analysis found: C, 75.32; H, 4.72; N, 8.69%. $C_{20}H_{15}FN_2O$ requires: C, 75.45; H, 4.75; N, 8.80%.

Preparation of 2-(4-fluorophenyl)-5-hydroxy-1-phenylbenzimidazole (PFHB) (***20***). To compound **18** (2.36 g, 0.0074 mol) contained in a 250 ml, round-bottom flask were added 48% hydrobromic acid (30 ml) and acetic acid (15 ml). The reaction mixture was heated at reflux for 6 h and then allowed to cool to room temperature. The crystals that formed were collected by filtration, washed with a 5% aqueous sodium bicarbonate solution, and then recrystallized from aqueous ethanol to afford 1.55 g (68% yield) of white needles (m.p. of 259–261°C). The i.r.(KBr) spectrum showed a peak at 1600 cm^{-1} (C=N), and the ^{1}H n.m.r. (DMSO-d^6) spectrum peaks at $\delta = 9.3$ (s, OH, 1H) and 7.6–6.7 ppm (m, aromatic, 12H). Elemental analysis found: C, 74.66; H, 4.28; N, 9.09%. $C_{19}H_{13}FN_2O$ requires: C, 74.99; H, 4.30; N, 9.21%.

Preparation of 6-fluoro-2-(4-hydroxyphenyl)-3-phenylquinoxaline (***22a***) *and 6-fluoro-3-(4-hydroxyphenyl)-2-phenylquinoxaline* (***22b***). To a 1 l, round-bottom flask, equipped with an overhead stirrer and a condenser, were added 4-hydroxybenzil (73.12 g, 0.3232 mol), 1,2-diamino-4-fluorobenzene (40.77 g, 0.3232 mol), chloroform (500 ml) and trifluoroacetic acid (1 ml). The reaction mixture was stirred and heated at reflux for 5 h, after which time it was allowed to cool to room temperature, washed with water, and then dried over magnesium sulfate. The solvent was removed under reduced pressure, and the residue was recrystallized from 85% ethanol to yield 92.97 g (91% yield) of a yellow powder, with m.p. of 110–130°C (cf. literature m.p. of 82–117°C[8]). The ^{1}H n.m.r. ($CDCl_3$) spectrum showed peaks at $\delta = 8.7$ (s, OH, 1H) and 8.1–6.7 ppm (m, aromatic, 12H).

Model compound syntheses

Preparation of 2-(4-fluorophenyl)benzimidazole (FB) (***27***). To a 500 ml, three-necked, round-bottom flask, equipped with an overhead stirrer, a condenser and a nitrogen inlet, were added 1,2-diaminobenzene (7.56 g, 0.0699 mol) and PPE (70 g). The reaction mixture was heated at 100°C, with stirring, until the diamine had completely dissolved, and then 4-fluorobenzoic acid (8.83 g, 0.0630 mol) was added. The mixture was stirred and heated at 120°C for 1 h, was allowed to cool to room temperature, and then poured into water (500 ml). The precipitate that formed was collected by filtration and dried in air, and the solid extracted with diethyl ether. The extract was reduced to dryness on a rotary evaporator, and the residue was finally sublimed to give 8.03 g (60% yield) of a white powder, with m.p. of 256–258°C (cf. literature m.p. of 260°C[17]). The ^{1}H n.m.r.

(acetone-d^6) spectrum showed peaks at $\delta = 8.3-7.2$ ppm (m, aromatic, 8H).

Preparation of 5(6)-fluoro-2-phenylbenzimidazole (**32**). This material was prepared by the reaction of compound **9** with benzoic acid using the procedure described above for compound **27**. The crude product was sublimed to give 4.93 g (61% yield) of a white powder (mp 243–245°C). The ^{1}H n.m.r. (acetone-d^6) spectrum showed peaks at $\delta = 8.2-7.0$ ppm (m, aromatic, 8H).

Polymerizations

Polymerization of FHB in NMP. To a 100 ml, four-necked, round-bottom flask, fitted with an overhead stirrer, a condenser, a nitrogen inlet and a Dean–Stark trap, were added FHB (2.2822 g, 10.000 mmol), NMP (20 ml), toluene (10 ml) and pulverized anhydrous K_2CO_3 (0.8984 g, 6.500 mmol). The reaction mixture was heated, with stirring, at 150°C for 6 h under nitrogen, and during this period the water that formed was collected in the Dean–Stark trap. As the reaction mixture was heated to 190°C toluene was removed by distillation. During this time the product began to precipitate. The mixture was heated at 190°C for 10 h and then at 200°C for a further period of 10 h. The dark brown reaction mixture was diluted with NMP (20 ml), allowed to cool to room temperature, and then added dropwise to methanol (500 ml) containing acetic acid (50 ml). The resulting tan-coloured powder was collected by filtration, air dried, and then refluxed twice, with stirring, first in methanol and then in water. The product was dried for 48 h at 100°C, under reduced pressure.

Polymerization of FHB in CHP. To a 100 ml, four-necked, round-bottom flask, fitted with an overhead stirrer, a condenser, a nitrogen inlet and a microdistillation head, were added FHB (2.2822 g, 10.000 mmol), CHP (20 ml) and pulverized anhydrous K_2CO_3 (0.8984 g, 6.500 mmol). (FB, 0.0106 g, 0.050 mol, was added to some polymerizations.) The reaction mixture was heated, with stirring, at 150°C for 6 h. During this period the reaction flask was purged with nitrogen to remove the water that was formed. The reaction mixture was then heated at 190°C for 6 h, and finally at 230 to 250°C for a further period of 24 h. The dark brown mixture was diluted with NMP (20 ml), allowed to cool to room temperature, and then added to methanol (500 ml) containing acetic acid (50 ml). The tan-coloured powder that precipitated was collected by filtration, air dried, and then refluxed twice with stirring, first in methanol and then in water. The final product was dried for 48 h at 100°C, under reduced pressure.

Polymerization of FHB in DPS. To a 100 ml, four-necked, round-bottom flask, fitted with an overhead stirrer, a condenser, a nitrogen inlet and a microdistillation head, were added FHB (2.2822 g, 10.000 mmol) and DPS (20 g). The reaction mixture was heated, with stirring, to 150°C, and when the solution became clear, pulverized anhydrous K_2CO_3 (0.8984 g, 6.500 mmol) was added to the system. The reaction mixture was stirred at 150°C for 6 h, then at 200°C for 6 h, and finally at 260–320°C for a further 10 h. The water that formed was removed by purging with nitrogen. The mixture was added to a blender containing acetone (200 ml) and acetic acid (20 ml), and the tan-coloured powder that precipitated was collected by filtration, air dried, and then refluxed twice, with stirring, first in methanol and then in water. The insoluble product was dried for 48 h, under reduced pressure.

Polymerization of monomers 7, 12 and 20 (PFHB). These monomers were polymerized in CHP using an identical procedure to that described above for FHB.

Copolymerization of FHB with PFHB. To a 100 ml, four-necked, round-bottom flask, fitted with an overhead stirrer, a condenser, a nitrogen inlet and a microdistillation head, were added FHB (1.1411 g, 5.000 mmol), PFHB (1.5216 g, 5.000 mmol), FB (0.0106 g, 0.050 mmol), CHP (20 ml) and pulverized anhydrous K_2CO_3 (0.8984 g, 6.500 mmol). The copolymerization was then carried out by the procedure described above for the homopolymerization of FHB.

Copolymerization of FHB with the A-B PPQ monomer ***22a,b***. The copolymerization of FHB with the isomeric monomer mixture **22a,b** was carried out in CHP by the procedure described above for the copolymerization of FHB with PFHB.

General procedure for the compression moulding of PBI powders

After drying at 100°C for 24 h, PBI powder (3.00 g) was placed in a compression mould (with dimensions of $32 \times 57 \times 0.32$ mm), which was then heated to 400°C in a hot press, using a heating rate of 1.5°C min^{-1}, and a moulding pressure of ~17 MPa. The mould was heated at 400°C for 0.5 h and then allowed to cool to room temperature.

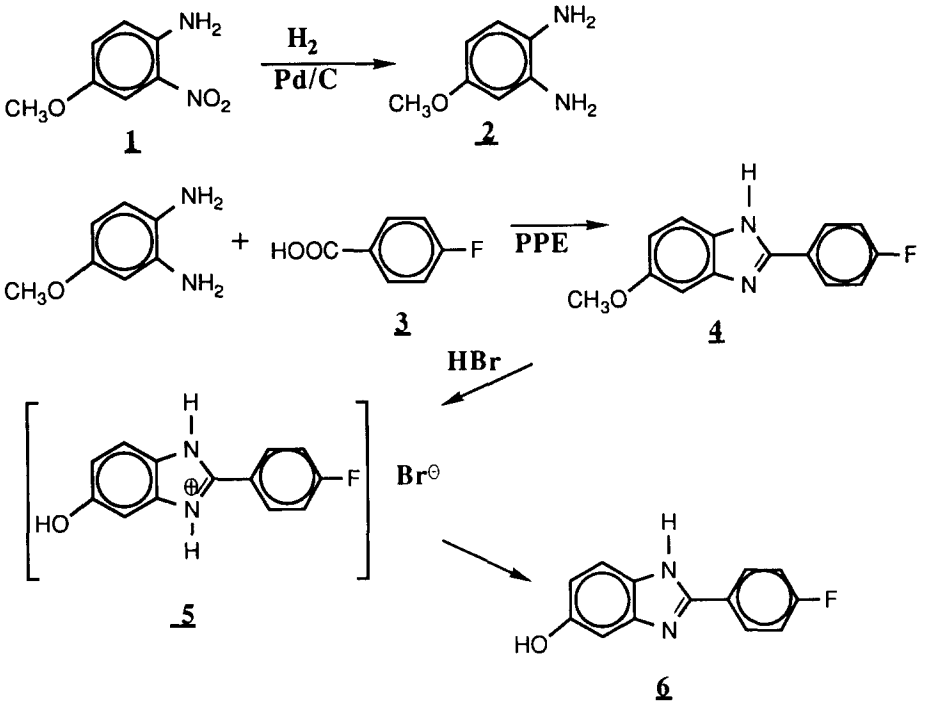
General procedure for film casting and the determination of mechanical properties

A sample of polymer (2.00 g) was dissolved in NMP (18.00 g) to give a 10 wt% solution, which was then carefully transferred onto a clean glass plate and stored under ambient conditions overnight. The solvent was then removed by heating successively at 100°C for 2 h, at 200°C for 2 h, and at 250°C for 1 h, under reduced pressure. After cooling to room temperature, the glass plate was immersed in water. The film was peeled from the glass plate and cut into dumb-bell-shaped specimens with a micro-dumb-bell cutting die, to produce specimens having widths and thicknesses of 2.4 cm and approximately 0.03–0.04 mm, respectively. Stress–strain data were obtained on an Instron Model 1130 Universal Testing Machine with a full-scale load of 5 kg, a crosshead speed of 5 mm min^{-1}, and a chart speed of 5 cm min^{-1}. The dumb-bell-shaped specimens were pulled at a strain rate of 0.3 min^{-1}.

RESULTS AND DISCUSSION

Monomer syntheses

The first A-B PBI monomer selected for synthesis was 2-(4-fluorophenyl)-5(6)-hydroxybenzimidazole (FHB) (**6**). The synthetic route used to prepare this monomer is shown in *Scheme 1*. Thus, 1,2-diamino-4-methoxybenzene (**2**) was obtained from the hydrogenation of 4-methoxy-2-nitroaniline (**1**) in the presence of palladium on



Scheme 1

activated carbon. Because the diamine was very susceptible to oxidation, it was purified by distillation under reduced pressure, immediately before being treated with 4-fluorobenzoic acid (**3**) in polyphosphate ester (PPE). The latter material, which was used as both the solvent and the dehydrating agent, was obtained from the reaction of P_2O_5 with diethyl ether in chloroform[13]. The yield of 2-(4-fluorophenyl)-5(6)-methoxybenzimidazole (**4**) was 45%. However, the product was contaminated with a small amount of PPE, which was detected by ^{1}H n.m.r. spectroscopy ($\delta = 3.8$ ppm). To remove the traces of PPE, the product was extracted with diethyl ether, the extract was evaporated to dryness, and the solid residue was purified by sublimation. The ^{1}H n.m.r. spectrum of **4** showed that this process successfully eliminated the PPE, although the carbon content of **4**, as determined by elemental analysis, was slightly lower (by 0.63%) than the calculated value. This difference was attributed to associated water in the compound. Problems have been encountered previously in obtaining correct elemental analyses for benzimidazoles[10]. Polyphosphoric acid (PPA) was also used as the solvent and the dehydrating agent, but in this case the reaction mixture gelled. Intermediate **4** was treated with 48% hydrobromic acid in acetic acid, which was heated at reflux. Upon standing at room temperature, the hydrobromide salt (**5**) crystallized from the reaction mixture. The salt was isolated and converted to FHB (**6**) by treatment with 5% aqueous sodium bicarbonate solution. The structure of FHB was ascertained by ^{1}H n.m.r. spectroscopy (*Figure 1*). However, the carbon content of this compound (as determined by elemental analysis) was 0.94% lower than the calculated value, again presumably due to associated water.

2-(2-Fluorophenyl)-5(6)-hydroxybenzimidazole (**7**), an isomer of FHB, was then synthesized using a slight modification of the route described for FHB. In this case, 2-fluorobenzoic acid was used in place of 4-fluorobenzoic acid.

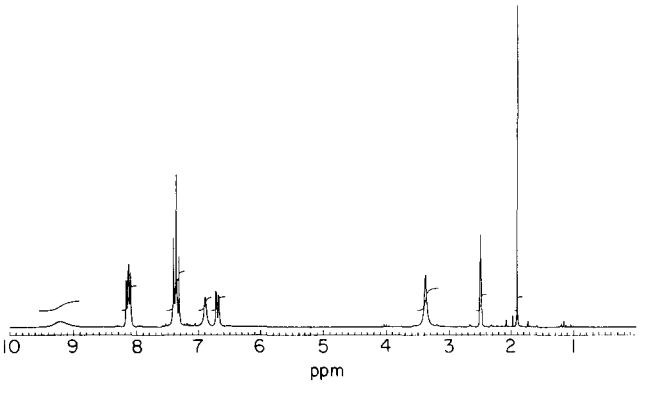
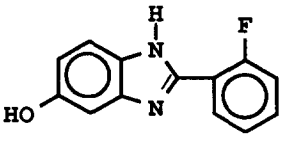


Figure 1 ^{1}H n.m.r. spectrum (DMSO-d^6) of 2-(4-fluorophenyl)-5(6)-hydroxybenzimidazole (FHB)



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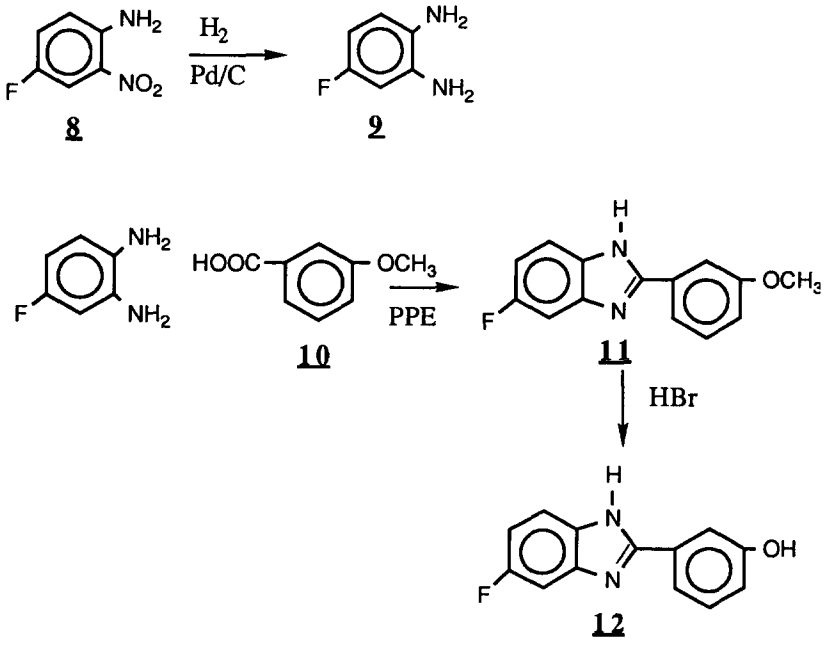
In order to obtain a monomer that would provide *meta*-catenation in a PBI, 5(6)-fluoro-2-(3-hydroxyphenyl)benzimidazole (**12**) was prepared by the synthetic route shown in *Scheme 2*. Thus, 4-fluoro-2-nitroaniline (**8**) was hydrogenated to 1,2-diamino-4-fluorobenzene (**9**) in the presence of palladium on activated carbon. Because this diamine was also very susceptible to oxidation, it was purified by sublimation before being treated with *m*-anisic acid (**10**) in PPE. The intermediate, 5(6)-fluoro-2-(3-methoxyphenyl)benzimidazole (**11**), was cleaved to **12** with 48% hydrobromic acid.

In order to obtain a monomer that would provide a phenylated PBI, 2-(4-fluorophenyl)-5-hydroxy-1-phenylbenzimidazole (PFHB) was prepared by the synthetic



Scheme 2

route shown in *Scheme 3*. Thus, 4-methoxy-2-nitroaniline (**1**) was coupled with bromobenzene (**13**), using copper powder as a catalyst. The copper powder was obtained from the reduction of $CuSO_4$ with Zn[14]. This copper-assisted nucleophilic substitution of an aryl halogen group required a high temperature and a tenfold excess of bromobenzene. The crude product, which was contaminated with several by-products and unreacted 4-methoxy-2-nitroaniline, was purified by chromatography on silica gel using a 90:10 (by volume) hexane/ethyl acetate mixture. The nitro-substituted intermediate **14** was hydrogenated to 2-amino-4-methoxydiphenylamine (**15**) over palladium on activated carbon. Again because of susceptibility to oxidation, **15** was distilled under reduced pressure before being treated with 4-fluorobenzoyl chloride (**16**) in DMAc in the presence of triethylamine. The yield of *N*-(4-fluorobenzoyl) 2-amino-5-methoxydiphenylamine (**17**) was 92%. This intermediate was converted to 2-(4-fluorophenyl)-5-methoxy-1-phenylbenzimidazole (**18**) in 80% yield by heating at 250°C under reduced pressure for 6 h. The conversion was followed by i.r. spectroscopy by monitoring the disappearance of the amide absorption band at 1680 cm^{-1} and the appearance of the imidazole absorption band at 1590 cm^{-1}. Intermediate **18**, which was purified by sublimation, was hydrolysed in 48% hydrobromic acid to afford the hydrobromide salt of 2-(4-fluorophenyl)-5-hydroxy-1-phenylbenzimidazole (**19**). This salt was then converted to **20** in 68% yield by treatment with 5% aqueous sodium bicarbonate solution. The structure of the product, which was recrystallized from aqueous ethanol, was ascertained by ^1H n.m.r. spectroscopy (*Figure 2*).

An A-B-type PPQ monomer was synthesized for copolymerization studies (*Scheme 4*)[8]. Thus, 4-hydroxybenzil (**21**) was treated with 1,2-diamino-4-fluorobenzene (**9**) in chloroform in the presence of trifluoroacetic acid. The product consisted of a mixture of two isomers, i.e. 6-fluoro-2-(4-hydroxyphenyl)-3-phenylquinoxaline (**22a**) and 6-fluoro-3-(4-hydroxyphenyl)-2-phenylquinoxaline (**22b**). The melting point of the isomer mixture, which

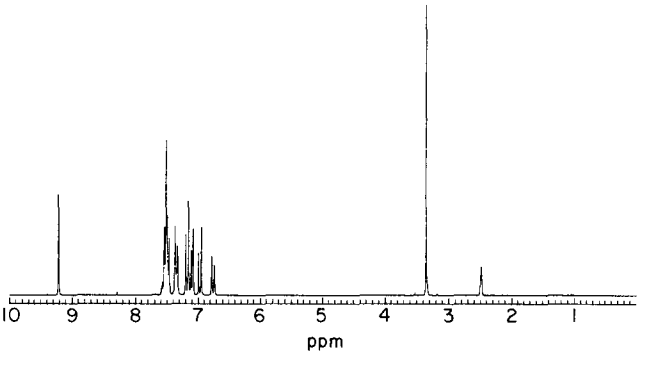


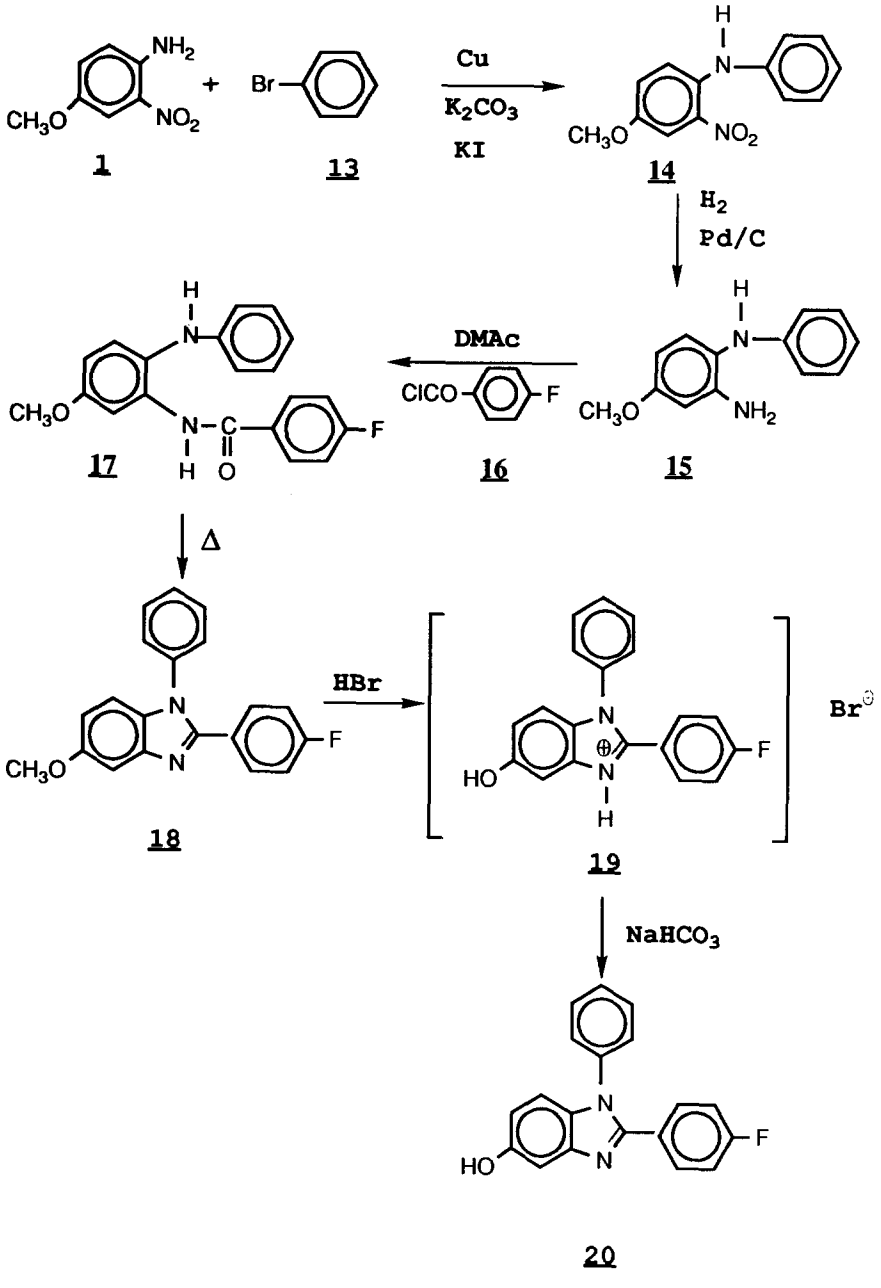
Figure 2 ^1H n.m.r. spectrum (DMSO-d^6) of 2-(4-fluorophenyl)-5-hydroxy-1-phenylbenzimidazole (PFHB)

resulted from two possible modes of addition of the diamine to the benzil, was very broad.

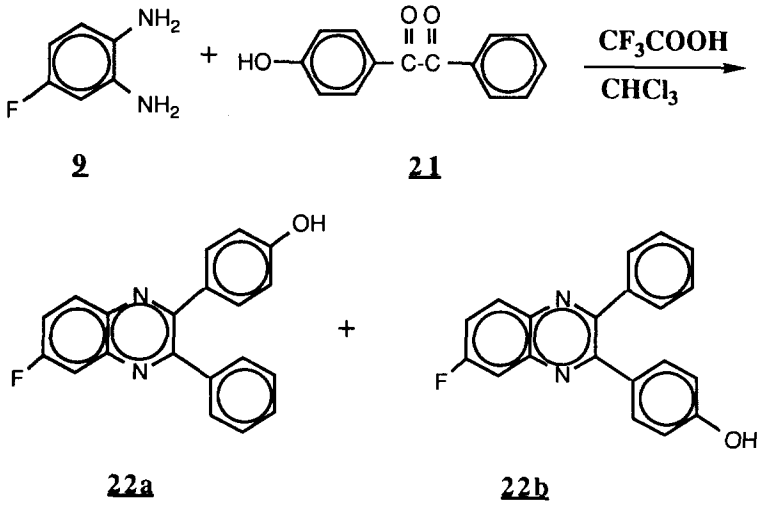
Polymerizations

The A-B PBI monomer FHB (**6**) was initially polymerized in NMP containing K_2CO_3 (*Scheme 5*), with toluene being used as an azeotroping agent. This polymerization was carried out in two steps. In the first step, the reaction mixture was heated at 150°C for 5 h to convert the hydroxyl group to the phenate salt, and in the second step, the reaction mixture was heated at 190°C to remove the toluene azeotrope and to effect polymerization. However, after approximately 2 h, the product precipitated. The intrinsic viscosity of the PBI thus obtained was only 0.33 dl g^{-1}. This low value of the viscosity was attributed to a premature precipitation of the propagating species.

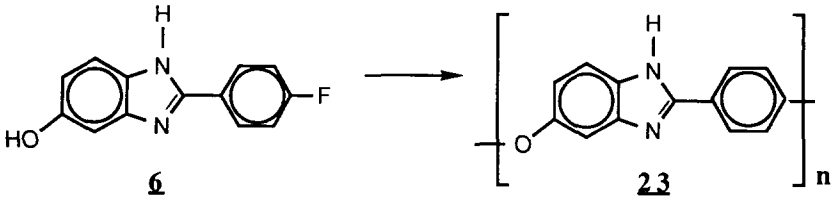
The polymer's insolubility was partially due to the presence of a small amount of toluene, which is not a solvent for PBI. Therefore, the toluene was replaced with *N*-cyclohexyl-2-pyrrolidinone (CHP). CHP is immiscible with water above 80°C so it can also serve as a dehydrating agent. In this case, the propagating species stayed in the solution throughout the polymerization,



Scheme 3



Scheme 4



Scheme 5

but the intrinsic viscosity of the resulting polymer, however, was still low, i.e. only 0.38 dl g^{-1}. It was postulated that higher-molecular-weight PBI might be obtained if the reaction temperature was increased to above 200°C. Thus, CHP was used as both the dehydrating agent and the solvent, and the polymerization was carried out at temperatures of 230 and 250°C. Although the propagating species precipitated out in approximately 2 h, it redissolved as the polymerization continued. The intrinsic viscosities of the PBIs prepared under these conditions ranged from 1.6 to 2.6 dl g^{-1}. In an attempt to further increase the molecular weight, polymerizations were carried out at temperatures between 260 and 320°C in DPS. All of the products produced under these reaction conditions were insoluble. It is known that hydrogen atoms *ortho* to a halogen can be removed by base at high temperature[18], and thus, they can serve as branching and crosslinking sites.

The d.s.c. thermogram of the PBI contained a small baseline shift near 355°C, which was tentatively identified as a T_g. In order to further clarify the position of this T_g, the PBI was compression moulded at 400°C, and the moulded product was then fabricated into a sample (of dimensions 1.26 × 5.0 × 8.0 mm) suitable for d.m.t.a. studies. The d.m.t.a. thermogram had a clear tan δ peak at 365°C (*Figure 3*). However, the decrease in the storage modulus at this point was small, which suggested the presence of crystallinity. Wide-angle X-ray diffraction (WAXD) analysis of powder samples showed that the PBI was semicrystalline (*Figure 4*), with the WAXD patterns giving an estimated degree of crystallinity of about 30%. Several PBIs with symmetrical structures have previously been found to be semicrystalline[11]. The polymer's t.g.a. thermograms showed 5% weight losses, at 460°C in air, and at 560°C in nitrogen (*Figure 5*). Since neither d.s.c. nor d.m.t.a. investigations gave any indication of melting below 460°C, the melting point of the PBI must lie above its decomposition temperature.

The PBI was slightly soluble in NMP, and highly viscous solutions could be prepared that contained up to 5 wt% solids. Although thin films could be cast from these solutions, they were very brittle. Since the intrinsic viscosity value of 2.6 dl g^{-1} indicated that the polymer had a high molecular weight, the brittleness of the films must be associated with the crystallinity of the PBI.

As stated earlier, the heterocyclic imidazole moiety in FHB acts as an electron-withdrawing group that activates the leaving group. It also stabilizes the Meisenheimer-type reaction intermediate **24** (*Scheme 6*). The phenoxide moiety, however, would be expected to decrease the activating power of the imidazole ring, and this would be particularly detrimental in the initial stage of polymerization. To investigate the effect of the phenoxide moiety on the initial displacement of fluorine,

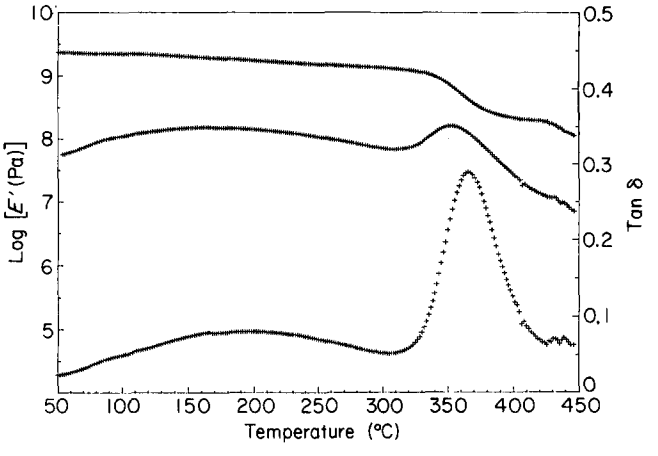


Figure 3 The d.m.t.a. thermogram of PBI measured in nitrogen using a heating rate of 1°C min^{-1}

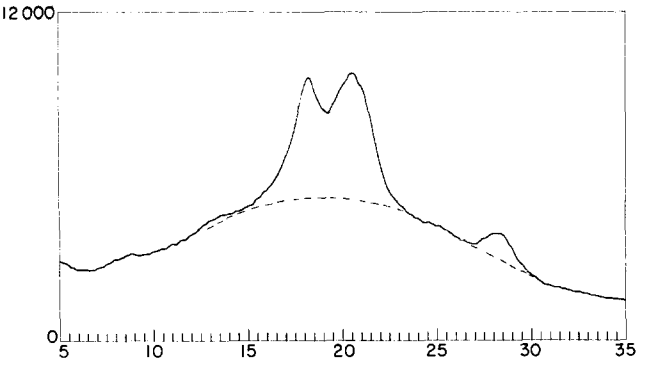


Figure 4 The WAXD pattern of a powder sample of PBI

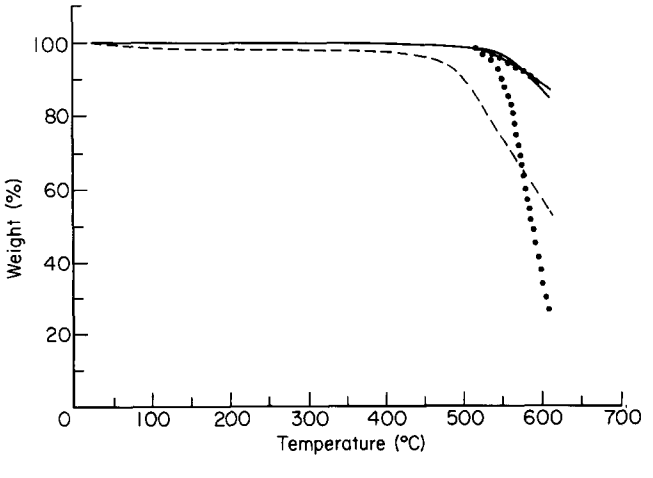
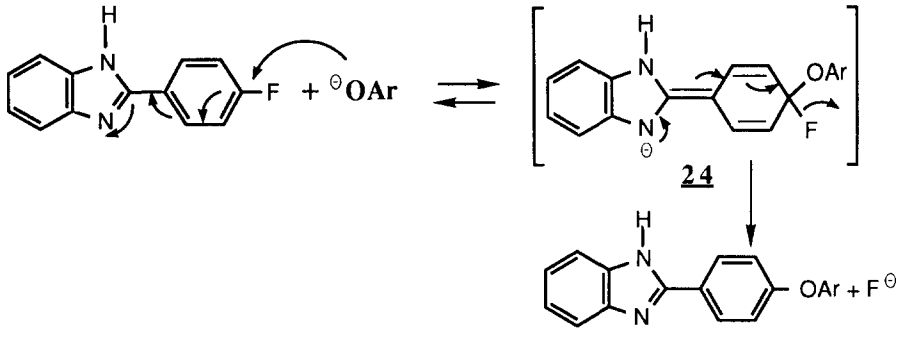
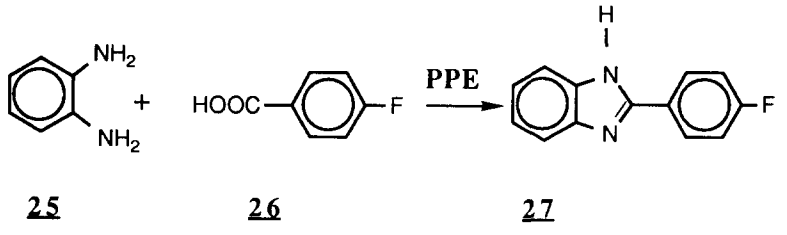


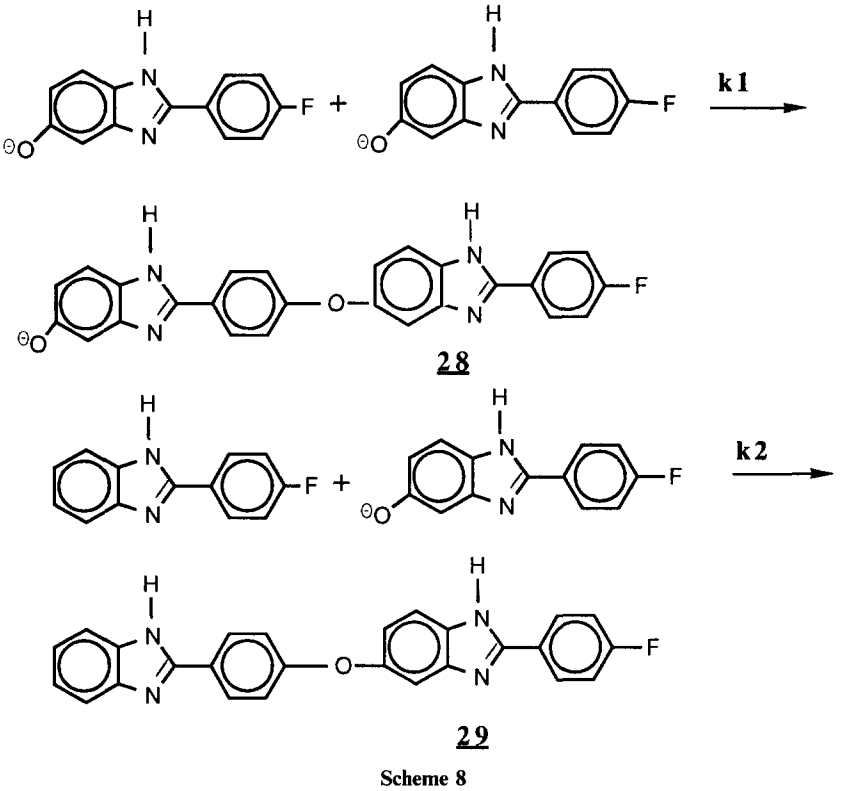
Figure 5 The t.g.a. thermograms of: PBI, measured in air (– – –) and in nitrogen (——) and; PPBI, measured in air (• • •) and in nitrogen (–•–•–•–). A heating rate of 10°C min^{-1} was used for all of the experiments



Scheme 6



Scheme 7



Scheme 8

2-(4-fluorophenyl)benzimidazole (FB) (**27**) was prepared by condensing 1,2-diaminobenzene (**25**) with 4-fluorobenzoic acid (**26**) in PPE (*Scheme 7*). The ^{19}F n.m.r. spectra of FB and FHB were then measured (*Figure 6*). The fluorine chemical shift in FB was 82.5 ppm as compared to 81.7 ppm for the fluorine atom in FHB, showing that the fluorine is not as subject to an electron-withdrawing effect in FHB as it is in FB[19]. This means that the rate of formation of the dimer **28** will be slower than that of the compound **29** (*Scheme 8*).

To determine if this effect was significant, 0.5 mol% of FB was added to a polymerization reaction of FHB,

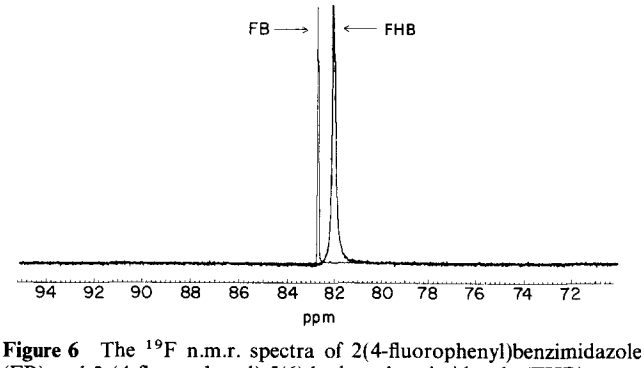
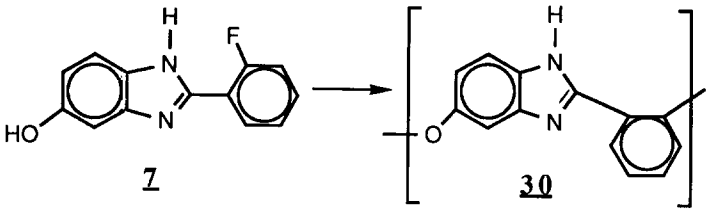
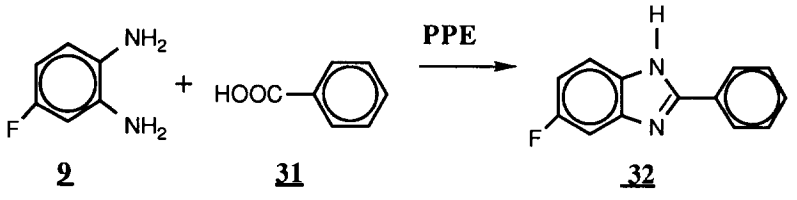


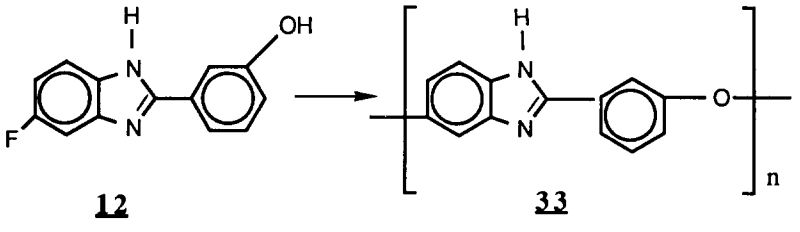
Figure 6 The ^{19}F n.m.r. spectra of 2(4-fluorophenyl)benzimidazole (FB) and 2-(4-fluorophenyl)-5(6)-hydroxybenzimidazole (FHB)



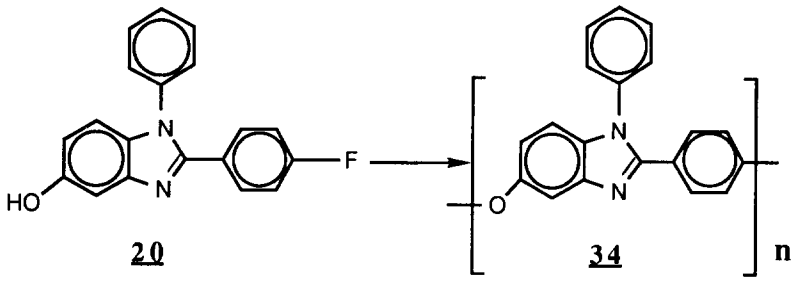
Scheme 9



Scheme 10



Scheme 11



Scheme 12

under the same reaction conditions. However, no significant differences were observed.

A study was next initiated to determine the effects of backbone catenation on the properties of the PBIs. In order to obtain an *ortho*-catenated polymer, 2-(2-fluorophenyl)-5(6)hydroxybenzimidazole (**7**) was polymerized in CHP, containing K_2CO_3, at 230°C over 24 h (*Scheme 9*). However, a very low molecular weight PBI was obtained by this procedure. Repeated runs produced material with intrinsic viscosities of less than 0.3 dl g^{-1}. Evidently, the nucleophilic attack at the *ortho*-position was too sterically hindered to allow for the build up of any significantly high-molecular-weight product.

Of particular interest was the incorporation of *meta*-catenation in the PBI backbone, as this is known to reduce T_g values and to increase solubility[11]. However, since the benzimidazole moiety in the initial A-B monomer structure primarily activated the *ortho*- and *para*-positions of the 2-phenyl ring for nucleophilic attack, a different type of structure had to be designed to obtain such catenation. It was postulated that the 5- and 6-positions of a benzimidazole structure would also be activated by the imidazole moiety. To test this hypothesis, 5(6)-fluoro-1-phenylbenzimidazole (**32**) was synthesized by condensing 1,2-diamino-4-fluorobenzene (**9**) with benzoic acid (**31**) (*Scheme 10*). The fluorine peaks in the ^{19}F n.m.r. spectrum of this compound occur at 71.8 and 73.8 ppm. A comparison of these chemical shifts with that of the fluorine in FB (**27**) (at 82.5 ppm) shows that the fluorine in **32** is not as activated for displacement. An attempt, however, was still made to polymerize 5(6)-fluoro-2-(3-hydroxyphenyl) benzimidazole (**12**) in CHP containing K_2CO_3 (at 230°C over 24 h) (*Scheme 11*), but only low molecular weight polymer was obtained. It is speculated that activation, by the imidazole moiety, of the 5- or 6-position is not sufficient to afford a high degree of nucleophilic substitution in these compounds.

In order to determine the effects of phenyl substitution on the properties of the PBIs, PFHB (**20**) was polymerized in CHP containing K_2CO_3, at 230°C for 10 h (*Scheme 12*). The intrinsic viscosity of the resulting

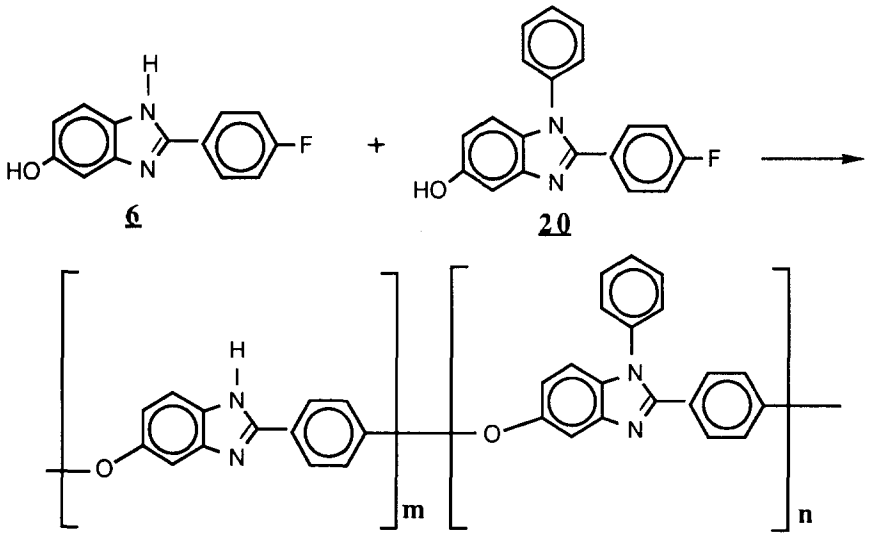
poly(*N*-phenylbenzimidazole) (PPBI), which stayed in solution throughout the polymerization, was 0.59 dl g^{-1}. In an attempt to increase the polymerization rate, the reaction was repeated in the presence of 0.5 mol% of FB. Although the polymerization was only allowed to proceed for 6 h at 230°C, the intrinsic viscosity of the PPBI that was obtained after this time was 1.2 dl g^{-1}. Thus, in contrast to the results obtained with FHB, the presence of the monofunctional FB material significantly affected the polymerization rate.

The d.s.c. thermogram of the polymer contained a large baseline shift near 278°C, indicative of a strong T_g, and a WAXD analysis showed that the polymer was completely amorphous. The polymer's t.g.a. thermograms showed 5% weight losses at 535°C in air and at 560°C in nitrogen (see *Figure 5*). Thus, the polymer had significantly better thermo-oxidative stability than its unphenylated analogue, while the thermal stability of the PPBI and the PBI were essentially identical. Vogel and Marvel[20] originally postulated that the thermo-oxidative stability of a PBI could be increased if the hydrogen atoms on the imidazole ring were replaced with phenyl groups. However, in the series of PPBIs that they prepared there were no significant differences between the thermo-oxidative and thermal stabilities of the phenylated polymers, and those of their unphenylated analogues. Korshak and coworkers[21] later prepared a series of PPBIs that had greater thermo-oxidative stability than their unphenylated counterparts, but they were less thermally stable.

The PPBI was quite soluble in NMP, and very viscous solutions could be prepared that contained up to 20 wt% solids. Thin, tough films were cast from 10% solutions; these films were cut into dumb-bell-shaped specimens (2.5 × 11.5 mm) and tested according to ASTM D-882. The films' tensile strengths were 100 MPa, and their i.r. spectra contained a strong absorption band due to aromatic C–H stretching at 3000 cm^{-1}, a C–N stretching band at 1600 cm^{-1}, and a C–O stretching band at 1200 cm^{-1}.

Copolymerizations

To obtain polymers with better mechanical properties and lower T_gs than that of the FHB homopolymer, FHB (**6**) was copolymerized with PFHB (**20**) (*Scheme 13*), with mole ratios of FHB and PFHB varying from 25:75 to 75:25 (*Table 1*). The polymerizations were carried out in CHP containing K_2CO_3, at a temperature of 230°C. FB (0.5 mol%) was added to increase the polymerization rate. The intrinsic viscosities of the resulting copolymers ranged from 1.09 to 1.55 dl g^{-1}. Their T_g values decreased as the amount of PFHB in the copolymer increased, but a corresponding improvement in the thermal stabilities of the copolymers was observed as their PFHB content increased.



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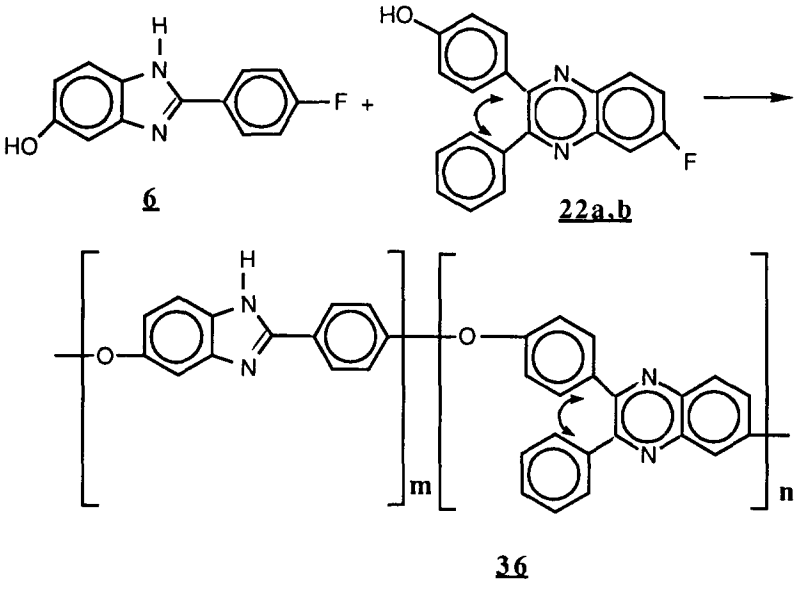
Scheme 13

Table 1 Properties of FHB/PFHB copolymers

Copolymer	Monomer feed ratio FHB (mol%)	PFHB (mol%)	$[\eta]^a$ (dl g^{-1})	$T_g{}^b$ (°C)	T.g.a. data[c] (°C) N_2	Air	Tensile strength[d] (MPa)
35a	75	25	1.55	342	535	498	57
35b	50	50	1.24	331	556	506	78
35c	25	75	1.09	296	563	503	85

[a]Intrinsic viscosity measured in NMP at 30°C
[b]Half height in baseline shift on d.s.c. thermogram obtained with a heating rate of 10°C min^{-1}
[c]Temperature at which 5% weight loss occurred with a heating rate of 10°C min^{-1}
[d]Determined on thin films according to ASTM D-882



Scheme 14

Table 2 Properties of FHB/A-B PPQ copolymers

Copolymer	Monomer feed ratio FHB (mol%)	Monomer feed ratio A-B PPQ (mol%)	$[\eta]^a$ (dl g^{-1})	$T_g{}^b$ (°C)	T.g.a. data[c] (°C) N_2	T.g.a. data[c] (°C) Air
36a	75	25	0.79	317	542	482
36b	50	50	0.80	307	543	598
36c	25	75	0.75	288	567	506

[a]Intrinsic viscosity measured in NMP at 30°C
[b]Half height in baseline shift on d.s.c. thermogram obtained with a heating rate of 10°C min^{-1}
[c]Temperature at which 5% weight loss occurred with a heating rate of 10°C min^{-1}

All the copolymers were soluble in NMP. Thin films were cast from 10 wt% NMP solutions, and then cut into dumb-bell-shaped specimens. As their PFHB content increased, the films became more flexible and their tensile strength increased (see *Table 1*). The films' i.r. absorption band at 3000 cm^{-1}, due to the phenyl group in PFHB, also became more intense.

In the second approach to obtaining polymers with better mechanical properties and lower T_gs than that of the FHB homopolymer, FHB was copolymerized with the A-B PPQ monomer mixture **22a,b** (*Scheme 14*), with mole ratios of FHB to A-B PPQ monomer varying from 75:25 to 25:75 (*Table 2*). The polymerizations were carried out in CHP containing K_2CO_3, at a temperature of 230°C. FB (0.5 mol%) was added to increase the polymerization rate. The intrinsic viscosities of the resulting copolymers ranged from 0.75 to 0.80 dl g^{-1}. Their T_g values decreased from 317 to 288°C as the PPQ content increased, while their thermal stabilities, as determined by t.g.a., were almost the same as that of the FHB homopolymer.

The copolymers were soluble in NMP. Thin films were cast from 10 wt% NMP solutions, but these films were very brittle and unsuitable for mechanical testing. As the films' PPQ content increased the i.r. absorption band at 3000 cm^{-1}, due to the phenyl group in the PPQ, became stronger.

SUMMARY AND CONCLUSIONS

Four new A-B PBI monomers containing a phenol moiety and a site activated for nucleophilic substitution by an imidazole ring have been prepared. The first monomer prepared, 2-(4-fluorophenyl)-5(6)-hydroxybenzimidazole (FHB), was converted to its phenate salt with K_2CO_3 and polymerized in NMP at 190°C, and in CHP at 230 to 250°C. Although low-molecular-weight material was obtained in NMP, PBI samples with intrinsic viscosities of 1.6 to 2.6 dl g^{-1} were obtained in CHP. Thus, at temperatures of 230 to 250°C imidazole activation of a fluorine atom located at the *para*-position of a 2-phenyl substituent results in a high degree of nucleophilic substitution. Attempts to polymerize FHB at higher temperatures in DPS resulted in crosslinking.

The PBI obtained from polymerization in CHP was semicrystalline, with a T_g near 365°C. The polymer possessed very good thermo-oxidative and thermal stability, and did not display a melting point below its decomposition temperature. The PBI was soluble in NMP and readily formed thin films from NMP solutions, but these films, however, were very brittle. This brittleness cannot be attributed to a low molecular weight. This surprising property may be associated with the polymer's crystallinity.

The second monomer, 2-(2-fluorophenyl)-5(6)-hydroxybenzimidazole, was also polymerized in CHP at 230 to 250°C. However, only low-molecular-weight material was obtained in this case. Since the *ortho*-position on a 2-phenyl substituent should be activated by the imidazole ring at least as much as the corresponding *para*-position, nucleophilic attack at the former must be quite sterically hindered.

In the third monomer that was studied the relative positions of the fluorine leaving group and the phenate nucleophile were reversed. Thus, 5(6)-fluoro-2-(3-hydroxyphenyl)benzimidazole was prepared and polymerized in CHP at 230 to 250°C. The fact that only low-molecular-weight material was obtained indicates that the activation of the 5- or 6-position by the imidazole ring is not sufficient to afford a high degree of nucleophilic substitution.

In order to obtain phenylated PBIs, 2-(4-fluorophenyl)-5-hydroxy-1-phenylbenzimidazole (PFHB) was synthesized and polymerized in CHP at 230 to 250°C. The rate of polymerization was significantly enhanced by the addition of 0.5 mol% of 2-(*p*-fluorophenyl)benzimidazole (FB). This additive was used to facilitate the initiation stage of the polymerization process. The poly(*N*-phenylbenzimidazole) (PPBI) obtained in this way was amorphous with a T_g near 278°C, which is 87°C lower than that of the unsubstituted PBI, indicating that the contribution of intermolecular hydrogen bonding to the T_g of the PBI is quite significant. Phenylation also increased the thermo-oxidative stability of the polymer. The 5% weight loss, observed on the PPBI's t.g.a. thermogram, occurred at 535°C in air, as opposed to 460°C for PBI. The PPBI was very soluble in NMP and readily formed tough, flexible films from these solutions, in marked contrast to the brittle films that were formed from solutions of PBI. The PPBI films had tensile strengths of 100 MPa.

In order to lower the T_g and to improve the mechanical properties of the FHB homopolymer, PFHB was copolymerized with FHB. The T_gs of the copolymers decreased from 342 to 296°C as their PFHB content increased from 25 to 75 mol%. The tensile strengths of thin films of these copolymers increased as their PFHB content increased.

In another attempt to improve the mechanical properties of the FHB homopolymer, FHB was copolymerized with an A-B PPQ monomer. The T_gs of the copolymers decreased from 317 to 288°C as their PPQ content increased from 25 to 75 mol%. Thin films of the copolymers, however, were brittle and similar to those of the PBI homopolymer. Thus, the preferred route to improving the mechanical properties of the PBI homopolymer was through the incorporation of phenylated repeat units.

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