Poly(aryl ether benzimidazoles)

R. Twieg, T. Matray, and J. L. Hedrick*

IBM Research Division, Almaden Research Center, 650 Harry Road, San Jose, California 95120−6099

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ABSTRACT: A method for the preparation of poly(aryl ether benzimidazoles) has been developed where the generation of an ether linkage is the polymer-forming reaction. We found that 2-(4-fluorophenyl)-benzimidazoles were activated toward nucleophilic aromatic substitution with phenoxides. Facile displacement occurred at this position since the benzimidazole ring can stabilize the negative charge developed in the transition state through a Meisenheimer complex, analogous to conventional activating groups (e.g., sulfone or carbonyl). An appropriately substituted dihalo bibenzimidazole, 2,2′-bis(4-fluorophenyl)-6,6′-bibenzimidazole, was prepared and polymerized with bisphenols in aprotic dipolar solvents in the presence of K_2CO_3. High molecular weight polymers were obtained with glass transition temperatures ranging from 220 to 250 °C. The resulting polymers were processable from solution and showed good thermal stability. This general synthetic route was also applied to AB monomers which, once polymerized, produced high polymer. This synthetic route affords the poly(benzimidazole) analogue of poly(ether imide) and shows many of the same desirable characteristics.

The aromatic poly(benzimidazoles) (PBI) comprise a class of heterocyclic polymers that show excellent thermal stability.[1] The high degree of molecular rigidity in the backbone together with intramolecular interactions produces a high-modulus polymer with a variety of applications including fibers and circuit boards. In spite of these attractive properties, the use of PBIs has been somewhat limited since many are only soluble in strong acids and cannot be processed from organic solvents. Improved solubility and processability have been accomplished by the incorporation of meta-substituted linkages, aryl ether linkages, and both pendent and main-chain alkyl substituents which can be built into the monomers prior to polymerization. The poly(benzimidazoles) are a subset of the group of poly-(benzazoles) which also includes the benzoxazole and benzthiazole heterocycle containing analogs.

The PBIs are generally synthesized by the step growth polymerization of an aromatic bis(*o*-phenylenediamine) with an aromatic diacid (or diacid derivative such as a diacid chloride). These polymerizations are often run in poly(phosphoric acid) (PPA) as this medium solvates the monomers and the subsequent polymer formed, activates both functional groups toward condensation, and reacts with the water formed by the polycondensation to effectively dehydrate the system.[2] An alternative synthesis method for the poly(benzazoles) is available when diaryl ether linkages are present in the polymer backbone. It has been generally recognized that incorporation of aryl ether linkages into a polymer backbone provides improved solubility and sustains many of the desired thermal and mechanical properties. As such, these polyethers are then attractive from both a synthetic and functional viewpoint. Using this polyether approach, the preformed heterocyclic unit is already fully elaborated in one (or both) of the comonomers which are combined in the final polyether synthesis.

Examples of high-temperature heterocycle-containing polymers which have been modified by the incorporation of aryl ether linkages include imides,[3] phenylquinoxalines,[4,5] triazoles,[6,7] benzoxazole,[8,9] oxadiazoles,[10,11] benzothiazoles,[12] isoquinolines,[13] and phthalazines.[14] Recently, the synthesis of many of these polymers was accomplished by heterocycle ring activated aromatic nucleophilic substitution chemistry involving displacement of an aryl halide with a phenoxide in a polar solvent. Conventional activating groups for aromatic nucleophilic substitution are simple electron-withdrawing groups such as ketone or sulfone, but it is now widely recognized that appropriately substituted heterocycles also can activate halides toward displacement. The characteristics common to all these activating groups is that they are electron withdrawing, usually have a site of unsaturation, and can stabilize the negative charge developed in the displacement through resonance to a heteroatom involving the formation of a Meisenheimer complex.

The effectiveness of a heterocycle as an electron-withdrawing group to activate nucleophilic displacement of aryl fluorides with phenoxides can be estimated by several methods. One method is computational and utilizes Hückel molecular orbital calculations (HMO)[13,14] to predict the partial positive charge density (δ) at the carbon bearing fluorine. As expected, the larger the value (δ), the higher is the reactivity. The other method is spectroscopic and involves using ^{1}H-NMR chemical shifts of the hydrogens ortho to the electron-withdrawing group as an indicator of the activating potential.[4] In general, a downfield shift corresponds to an increase in the reactivity. It is important to realize that these two methods of determining reactivity only consider *inductive* effects of the activating group and do not take into account the extent to which the activating group stabilizes the Meisenheimer complex intermediate. The polymerizations require the use of dipolar aprotic solvents such as *N*-methylpyrrolidone (NMP), dimethylacetamide (DMAC), dimethyl sulfoxide (DMSO), or *N*,*N*′-dimethylpropyleneurea (DMPU). DMPU has been shown to be beneficial in the cases where more rigid heterocycles are incorporated into poly(aryl ethers).[15]

Connell and co-workers have prepared poly(aryl ether benzimidazoles), where the preformed benzimidazole heterocycle was introduced in the bisphenol and polymerized with conventional activated bis(aryl halides) in the presence of base (AABB condensation).[16−18] The resulting polymers could be prepared in high molecular

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weight in common organic solvents and could be processed from solution or the melt. These polymers were shown to have exceptional thermal and mechanical properties. We have recently focused our efforts on the preparation and polymerization of benzoxazole and benzothiazole heterocycles which have 4-fluorophenyl groups pendent on the 2-position of the benzazole. Here the heterocycle acts as a conjugating and electron-withdrawing group activating the aryl fluoride toward aromatic nucleophilic substitution polymerization. Model reactions of sodium cresolate with either 2-(4-fluorophenyl)benzothiazole or 2-(4-fluorophenyl)benzimidazole previously published[19] demonstrated that the desired aryl ether linkage was prepared in high conversion, demonstrating the generality of benzazole-activation for poly(aryl ether) synthesis. Harris and co-workers[20] have used the benzazole activation in the synthesis of poly(benzimidazoles) via nucleophilic aromatic substitution of an AB monomer. High molecular weight polymer were obtained with significantly improved stability. In this paper, we will describe our investigation of imidazole-activated fluoro displacement as a route to PBIs containing aryl ether linkages, with the objective of extending the scope of heterocycle-activated halo displacements as well as obtaining PBIs that may be processed from common organic solvents or the melt. In most of these examples, polymer formation by aromatic nucleophilic substitution reaction is usually accomplished in an AABB fashion, e.g., between a bisphenol and a counterpart containing two 2-(4-fluorophenyl)benzazole units. It has previously been demonstrated by the preparation and self-polymerization of 6-fluoro-2-(4-hydroxyphenyl)-3-phenylquinoxaline that AB synthesis is an alternatie route to new poly(aryl ether phenylquinoxalines).[21] By utilizing this AB monomer, rigorous control of the stoichiometry, as required, for conventional poly(aryl ethers), was no longer necessary. In an analogous fashion to Harris and co-workers, we have now extended this AB strategy to 2-phenylbenzimidazoles in which the fluorine leaving group is on the para position of a benzene ring appended to the 2-position of the activating benzazole heterocycle and the phenolic functionality is also on the same monomer (directly on the annulated benzene ring of the benzazole or attached via some intervening structure).

Experimental Section

Materials. NMP, *N*-cyclohexylpyrrolidone (CHP), and DMPU were vacuum distilled over calcium hydride. The monomer 2,2-bis(4-hydroxyphenyl)propane (Aldrich) was recrystallized from toluene, and 2,2-bis(4-hydroxyphenyl)-hexafluoropropane (Aldrich) and 2,2′-bis(4-hydroxyphenyl)-diphenylmethane (Applied Organics) were recrystallized from toluene/ethyl acetate (95/5). The 3,3′-diaminobenzidine (Aldrich), poly(phosphoric acid) (Aldrich), and 4-fluorobenzoic acid (Aldrich) were used without further purification.

Monomer Synthesis. Synthesis of 2,2′-Bis(4-fluorophenyl)-6,6′-bibenzimidazole (1). The monomer 2,2′-bis-(4-fluorophenyl)-6,6′-bibenzimidazole (1) was prepared in a three-necked flask equipped with an overhead stirrer, condenser, and nitrogen inlet. The flask was charged with 3,3′-diaminobenzidine and 4-fluorobenzoic acid and carefully rinsed in with 220 mL of poly(phosphoric acid). It is important to note that the 4-fluorobenzoic acid was used in excess to ensure complete conversion. The reaction mixture was heated to 175 °C and maintained for 24 h. The reaction mixture was allowed to cool, precipitated in methanol, and isolated by filtration. The product was subjected to a number of both methanol and water rinses and then boiled in both water and methanol to remove both the poly(phosphoric acid) and unreacted 4-fluorobenzoic acid, respectively. The dark crude product was isolated in high yield (>90%) and recrystallization from either NMP or DMAC afforded a light tan powder: mp 340−345 °C. Anal. Calcd for $C_{26}F_2N_4H_{14}$: C, 73.92; H, 3.82; N, 13.26. Found: C, 73.20; H, 4.42; N, 12.32.

Synthesis of 1-Phenyl-2-(4-fluorophenyl)-6-(4-hydroxyphenoxy)benzimidazole (2). 2-Nitro-5-fluorodiphenylamine. In a 1000 mL round-bottom flask equipped with a stirbar, reflux condenser, and nitrogen inlet were placed 2,4-difluoronitrobenzene (95.45 g, 600 mmol), dimethyl sulfoxide (300 mL), aniline (69.8 g, 750 mmol), and anhydrous potassium carbonate (82.8 g, 600 mmol). The resulting slurry was gradually warmed to 90 °C and maintained at that temperature for 3 h. After this time only a trace of the starting difluoronitrobenzene remained so additional aniline (5 g, 53.7 mmol) was added and the reaction maintained an additional hour at 90 °C. The slurry was cooled and transferred to a 2 L Erlenmeyer flask with the aid of some water, and then 10% aqueous HCl was added dropwise with stirring until the total volume was 1800 mL. The orange precipitate was isolated by suction filtration, washed well with water, and recrystallized from a mixture of acetic acid and water to give 122.2 g (88%) of orange crystals in two crops: mp 90.0−92.2 °C; ^{1}H NMR ($CDCl_3$) δ 9.66 (br, s, 1H), 8.32−8.22 (dd, J = 6.0, 6.1 Hz, 1H), 7.49−7.39 (m, 2H), 7.35−7.20 (m, 3H), 6.85−6.77 (dd, J = 2.4, 2.7 Hz, 1H), 6.53−6.43 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 169.1, 165.0, 145.4, 137.7, 129.8, 129.5, 126.3, 124.8, 106.0, 105.6, 101.4, 100.9. Anal. Calcd for $C_{12}H_9N_2O_2F$: C, 62.07; H, 3.91; N, 12.06; F, 8.18. Found: C, 61.99; H, 3.83; N, 11.99; F, 7.93.

2-Nitro-5-(4-methoxyphenoxy)diphenylamine. In a 1000 mL round-bottom flask configured as before were put 2-nitro-5-fluorodiphenylamine (46.4 g, 200 mmol), *p*-methoxyphenol (27.28 g, 220 mmol), anhydrous potassium carbonate (30.36 g, 220 mmol), and 350 mL of *N*-methylpyrrolidinone. The mixture was heated to 130 °C amd stirred for 3 h. After cooling, 500 mL of 10% HCl was added dropwise, resulting in an oily residue. The mixture was extracted with ethyl acetate and washed with 300 mL of water and 300 mL of 10% HCl. The organic phase was dried and evaporated, giving a orange solid which was recrystallized from methanol to give 56.86 g (84.9%) of the product as orange crystals: mp 83−85 °C; ^{1}H NMR ($CDCl_3$) δ 9.71 (s, 1H), 8.17 (d, J = 9.5 Hz, 1H), 7.43−7.13 (m, 5H), 6.98 (d, J = 9.2 Hz, 2H), 6.89 (d, J = 9.1 Hz, 2H), 6.68 (s, 1H), 6.27 (d, J = 9.2 Hz, 2H), 3.80 (s, 3H). Anal. Calcd for $C_{19}H_{16}N_2O_4$: C, 67.85; H, 4.79; N, 8.33. Found: C, 68.16; H, 4.55; N, 8.33.

2-Amino-5-(4-methoxyphenoxy)diphenylamine. In a 500 mL round-bottom two-neck flask equipped with a stirbar, gas inlet, and reflux condenser (fitted with a balloon) were put 2-nitro-5-(4-methoxyphenoxy)diphenylamine (10.0 g, 30 mmol), 10% palladium hydroxide on activated carbon (1.0 g), and 90 mL of ethylene glycol dimethyl ether. The system was flushed with nitrogen two times by filling the balloon and allowing it to discharge through the flask. The same was done with hydrogen after which the second aperture was sealed with a septum. The balloon was refilled with hydrogen and the yellow solution was warmed to 40 °C and allowed to stir for 5 h. After this time only a small amount of starting material was found to remain by TLC analysis. The reaction was allowed to stand overnight at room temperature under hydrogen, resulting in a clear solution. The amine was not isolated but converted to its 4-fluorobenzamide derivative in situ.

***N*-(4-Fluorobenzoyl)-2-anilino-4-(4-methoxyphenoxy)-aniline.** The crude reduction mixture containing the 2-amino-5-(4-methoxyphenoxy)diphenylamine was swept with a stream of nitrogen to remove any remaining hydrogen, and then pyridine (2.37 g, 30 mmol) was added following by 4-fluorobenzoyl chloride (4.76 g, 30 mmol). The system was kept under nitrogen and allowed to stir for 2 h at room temperature. The mixture was then filtered (with the aid of some ethyl acetate) through a pad of silica gel, and the resulting solution was stripped of solvent, leaving 13.23 g of an off-white solid. This material was used without further purification: mp 125.6−126.6 °C; ^{1}H NMR (DMSO) δ 9.71 (br, s, 1H), 8.06−7.94 (m, 2H), 7.59 (br, s, 1H), 7.39 (d, J = 8.5 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 7.25−7.14 (m, 2H), 7.09−6.92 (m, 5H), 6.87−6.76 (m, 2H), 6.52 (d, J = 8.8 Hz, 1H), 3.74 (s, 3H).

1-Phenyl-2-(4-fluorophenyl)-6-(4-methoxyphenoxy)-benzimidazole. Into a 1000 mL round-bottom flask fitted with a stirbar, reflux condenser, and nitrogen inlet were put *N*-(4-fluorobenzoyl)-2-anilino-4-(4-methoxyphenoxy)aniline (13.25 g, 30 mmol) and 250 mL of acetic acid. The solution was heated to reflux (150 °C) for 3 h. After cooling, 750 mL of water was added dropwise, giving a cloudy mixture which was extracted with 300 mL of ethyl acetate and neutralized with sodium bicarbonate. The organic extract was dried, filtered, and evaporated, leaving a brown crystalline solid. Purification by low-pressure liquid chromatography (5−10% gradient of EtOAc/toluene) gave a white solid which was recrystallized from EtOH and water, leaving 6.94 g (56.1%) of white fluffy crystals: mp 134.2−136.1 °C; ^{1}H NMR ($CDCl_3$) δ 7.78 (d, J = 10.1 Hz, 1H), 7.61−7.46 (m, 5H), 7.41 (d, J = 6.7 Hz, 2H), 7.29−7.16 (m, 2H), 7.03−6.86 (m, 5H), 6.68 (s, 1H), 3.73 (s, 3H). Anal. Calcd for $C_{26}H_{19}N_2O_2F$: C, 76.08; H, 4.66; N, 6.82; F, 4.63. Found: C, 76.34; H, 4.56; N, 6.85; F, 4.42.

1-Phenyl-2-(4-fluorophenyl)-6-(4-hydroxyphenoxy)benzimidazole (2). Into a 500 mL round-bottom flask equipped with a stirbar, reflux condenser, and nitrogen inlet were put 2-(4-fluorophenyl)-3-phenyl-6-(4-methoxyphenoxy)benzimidazole (6.5 g, 15.8 mmol) and pyridine hydrochloride (45.5 g, 40 mmol). The solid mixture was heated to 190 °C, and after 4.5 h the solution was allowed to cool to a solid to which 500 mL of water was added. The resulting white precipitate was filtered and washed well with water. Recrystallization from a mixture of 2-propanol and water gave 4.86 g (77.6%) of white crystals. Anal. Calcd for $C_{25}H_{17}N_2O_2F$: C, 75.75; H, 4.32; N, 7.07; F, 4.79. Found: C, 75.38; H, 4.28; N, 7.20; F, 4.30.

Synthesis of 2-(4-Fluorophenyl)-5-(4-hydroxyphenoxy-)benzimidazole (3). 2-Amino-4-fluoronitrobenzene. In a 500 mL pear flask equipped with a stirbar, an addition funnel, and a nitrogen inlet were put 2,4-difluoronitrobenzene (31.8 g, 200 mmol) and *N*-methylpyrrolidinone (100 mL). The solution was stirred in a water bath and aqueous ammonia was added dropwise (20 mL over 20 min). After stirring for 15 h at room temperature, 20 mL more of aqueous ammonia was added dropwise. After 24 h, the reaction was still not complete so 50 mL of NMP and 20 mL of concentrated ammonium hydroxide were added. Six hours later TLC showed only a trace of the 2,4-difluoronitrobenzene left so the slurry was chilled in an ice bath and brought up to 500 mL with dropwise addition of ice water. The resulting yellow solid was isolated by suction filtration and washed well with water. Recrystallization from 2-propanol and water gave 30.0 g (96%) of yellow needles: mp 96 °C; ^{1}H NMR (DMSO) δ 8.11−8.02 (m, 2H), 7.61 (br, s, 2H), 6.67 (d, J = 10.7 Hz, 1H), 6.49 (t, J = 8.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 129.36, 129.17, 105.85, 105.46, 103.76, 103.35. Anal. Calcd for $C_6H_5FN_2O_2$: C, 46.16; H, 3.23; F, 12.17; N, 17.94. Found: 45.80; H, 3.24; F, 12.05; N, 17.58.

2-Amino-4-(4-methoxyphenoxy)nitrobenzene. Into a 500 mL round-bottom flask fitted with a stirbar, reflux condenser, and nitrogen inlet were put 2-amino-4-fluoronitrobenzene (10.0 g, 64.1 mmol), 4-methoxyphenol (8.74 g, 71 mmol), potassium carbonate (17.7 g, 128.2 mmol), and 150 mL of *N*-methylpyrrolidinone. The mixture was heated to 150 °C for 4 h in an oil bath, after which TLC showed the reaction had gone to completion. After cooling to room temperature, 350 mL of water was added dropwise, resulting in the formation of a yellow precipitate. Filtering, washing well with water, and recrystallizing from ethanol and water gave 15.13 g (97%) of yellow crystals: ^{1}H NMR ($CDCl_3$) δ 7.97 (d, J = 9.8 Hz, 1H), 7.45 (br, s, 2H), 7.11 (d, J = 9.1 Hz, 2H), 7.01 (d, J = 9.3 Hz, 2H), 6.29−6.2 (m, 2H), 3.77 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 164.3, 156.7, 148.4, 147.1, 128.3, 125.9, 122.2, 115.3, 106.5, 102.1, 55.5.

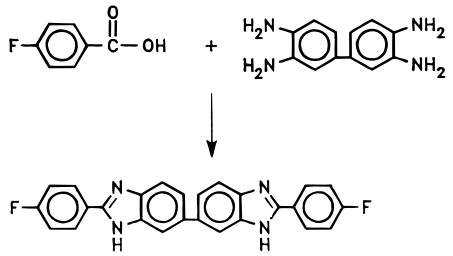
***N*-(4-Fluorobenzoyl)-2-nitro-5-(methoxyphenoxy)-aniline.** Into a 500 mL round-bottom flask fitted with a reflux condenser, nitrogen inlet, and stirbar were put 2-amino-4-(methoxyphenoxy)nitrobenzene (10.0 g, 41 mmol), 4-fluorobenzoyl chloride (6.49 g, 41 mmol), and 150 mL of pyridine. The solution was warmed in an oil bath to 40 °C and allowed to stir for 8 h. To complete the reaction, 3.0 g (17 mmol) and 4-fluorobenzoyl chloride was added and the solution was allowed to stir for 8 h more at 40 °C. Addition of 250 mL of water resulted in the formation of a yellow precipitate which was isolated by suction filtration and washed well with water. Recrystallization from ethanol and THF gave 11.63 g (77.8%) of yellow needles: ^{1}H NMR (acetone) δ 11.36 (br, s, 1H), 8.45 (s, 1H), 8.31 (d J = 9.4 Hz, 1H) 8.11−7.99 (m, 2H), 7.44−7.31 (m, 2H), 7.21−7.00 (m, 4H), 6.85−6.76 (m, 1H), 3.84 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 167.3, 165.2, 164.6, 163.3, 157.1, 147.3, 137.6 130.5, 129.8, 129.7, 128.4, 121.8, 116.2, 115.9, 115.2, 111.4, 107.9, 55.5

2-(4-Fluorophenyl)-5-(4-methoxyphenoxy)benzimidazole. Into a 500 mL round-bottom two-neck flask equipped with a stirbar, reflux condenser, and a gas inlet fitted with a balloon were put *N*-(4-fluorobenzoyl)-2-nitro-5-(methoxyphenoxy)aniline (10.0 g, 27 mmol), 10% palladium on activated carbon (1.0 g), and 150 mL of acetic acid. The system was flushed first with nitrogen and then with hydrogen, resulting in the balloon being filled with hydrogen. The reaction mixture was heated at 80 °C for 4 h and was then allowed to stir at room temperature for an additional 12 h. After this time, thin-layer chromatography showed the reaction was complete, and the system was flushed with nitrogen. The mixture was then filtered through a short bed of silica gel to remove catalyst and concentrated by rotoevaporation. Purification by silical gel chromatography (50% EtOAc/50% hexane) gave a white solid which was recrystallized from toluene and cyclohexane, giving 5.24 g (61%) of white needles: ^{1}H NMR ($CDCl_3$) δ 8.05−7.99 (m, 2H), 7.54 (d, J = 9.2 Hz, 1H), 7.19−7.07 (m, 3H), 7.01−6.82 (m, 5H), 3.80 (s, 3H).

2-(4-Fluorophenyl)-5-(4-hydroxyphenoxy)benzimidazole (3). In a 500 mL round-bottom flask equipped with a reflux condenser, nitrogen inlet, and stirrer were put 2-(4-fluorophenyl)-5-(4-methoxyphenoxy)benzimidazole (4.0 g, 12.6 mmol), and pyridine hydrochloride (30.0 g, 260 mmol). The mixture was heated to 175 °C for 7 h after which thin-layer chromatography indicated the reaction was complete. Addition of 500 mL of water resulted in the formation of a yellow precipitate which was purified by siilcal gel chromatography (50% EtOAc/50% hexane to 45% EtOAc/45% hexane/10% MeOH). The isolated solid was recrystallized from ethanol and water, giving 2.10 g (55%) of powdery needles: ^{1}H NMR (DMSO) δ 12.86 (br, s, 1H), 9.29 (br, s, 1H), 8.18−8.13 (m, 2H), 7.53−7.35 (m, 3H), 6.91−6.75 (m, 6H).

Polymer Synthesis. A typical synthesis of a poly(aryl ether benzoxazole) was conducted in a three-neck flask equipped with a nitrogen inlet, mechanical stirrer, Dean−Stark trap, and a condenser. A detailed synthetic procedure designed to prepare a poly(aryl ether benzimidazole) is provided. The flask was charged with **1** (3.4707 g, 6.0420 mmol) and Bisphenol-AF (2.0314 g, 6.0420 mmol) carefully washed into the flask with 25 mL of DMPU. Toluene (20 mL) and K_2CO_3 (1.25 g, 9.06 mmol) were added. Note that the K_2CO_3 was used in 40−50% excess. The reaction mixture was then heated until the toluene began to reflux. An optimum reflux temperature range was achieved when the oil bath was maintained between 150 and 170 °C. Toluene was periodically removed from the Dean−Stark trap and replaced with deoxygenated dry toluene to ensure dehydration. The reaction mixture was maintained at 160 °C until the presence of water was no longer observed in the Dean−Stark trap. This usually took between 4 and 8 h, and, during this stage of the reaction, the solvent underwent several color changes. For example, during the initial formation of the phenoxide, a yellow-brown color was observed and as the refluxing proceeded, the color changed to brown. Upon dehydration, the temperature was slowly increased to 180 °C and the toluene was removed through the Dean−Stark trap. The polymerization was heated at 180 °C for approximately 20 h, and completion or near completion was qualitatively estimated by the point where the viscosity increased dramatically. The high molecular weight product **4a** was diluted with 50 mL of NMP and filtered hot to remove the inorganic salts. The filtered solution was cooled, and several drops of weak acid (e.g., acetic acid) were added to neutralize the phenoxide end groups. The polymer solution was then coagulated in approximately 10× volume of methanol and then boiled in water to remove trapped salts. The polymer was then dried

Scheme 1



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in a vacuum oven (80 °C) to a constant weight. In each case the yield was essentially quantitative.

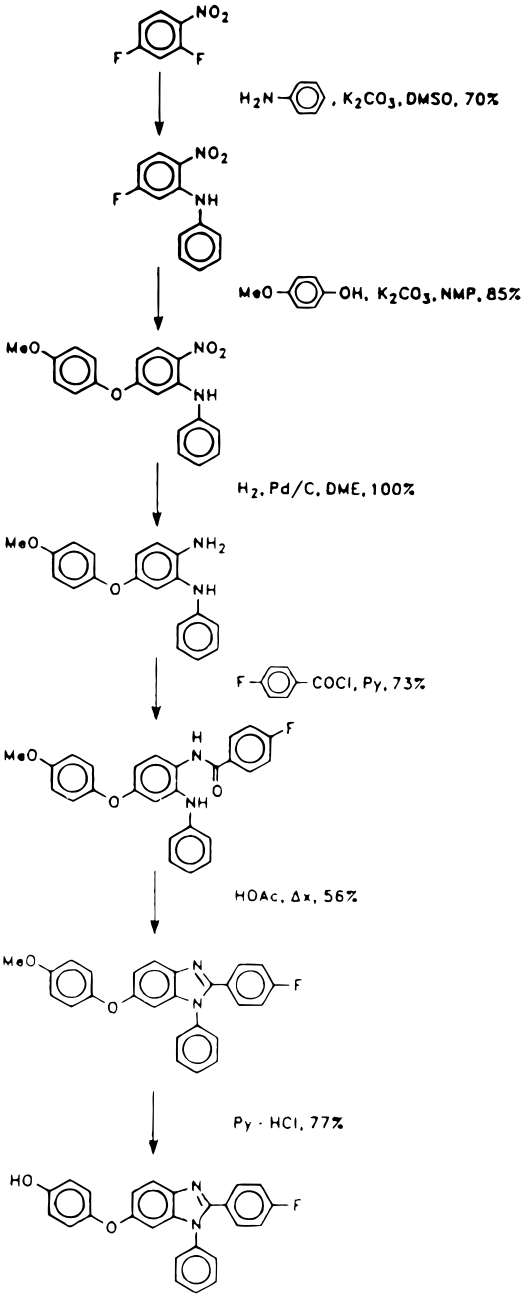
Characterization. Glass transition temperatures, taken as the midpoint of the change in a slope of the base line, were measured on a DuPont DSC 1090 instrument with a heating rate of 10 °C/min. Thermal gravimetric analysis (TGA) on the polymer films was conducted with a heating rate of 5 °C/min for the variable scans. Intrinsic viscosity measurements were determined by using a Cannon Ubbelohde dilution viscometer in NMP or CHP (25 °C).

Results and Discussion

The rationale for the benzazole-activated aromatic nucleophilic displacement is similar to that of the conventional systems in which the site of attack is polarized (made electron deficient) by both the leaving group and the activating group and the transition state is stabilized by having an efficient means for charge delocalization. The effectiveness of a benzazole as an activating group may be estimated by comparison of its group Hammett coefficients relative to other common activating groups. In fact, it is fortunate that Hammett coefficients for some of these benzazoles have already been determined.[20,21] These heterocycles have the following σ_p values when appended at their 2-positions (on the carbon between the two electronegative heteroatoms): benzoxazole, 0.34; benzthiazole, 0.34; *N*-phenylbenzimidazole, 0.24. These σ values are not particularly large but are in the range of those for typical carbonyl activating groups: PhCO, 0.46; PhNHCO, 0.35. For comparison, a very potent activating group is the phenyl sulfone system found in diphenyl sulfone polymers: $PhSO_2$, 0.70. The feasibility of the benzazole-activated fluoro displacement was first evaluated in model reactions of 2-(4-fluorophenyl)benzoxazole, 2-(4-fluorophenyl)benzothiazole, and 2-(4-fluorophenyl)benzimidazole with *m*-cresol in NMP containing base, affording the desired aryl ethers in each case in approximately 95% yields.[22] The reactions occurred with high conversion and yield, demonstrating the relevance of benzazole activation for poly(aryl ether) syntheses.

To survey the utility of the benzimidazole-activated fluoro displacement as a route to poly(aryl ether benzimidazoles), the appropriate bis(fluorophenyl)benzimidazole, **1**, was prepared. The 2,2′-bis(4-fluorophenyl)-6,6′-bibenzimidazole was prepared by the condensation of 3,3′-diaminobenzidine with 4-fluorobenzoic acid (Scheme 1). The reaction was mediated in PPA, since PPA solvated the starting materials and subsequent monomer as well as reacts with the water formed during condensation, effectively dehydrating the system. Thin-layer chromatography (TLC) showed the disappearance of the starting materials with the formation of a single product peak. The reaction was precipitated in methanol to remove unreacted 4-fluorobenzoic acid, and the product was isolated in high yield. The crude product was subject to several methanol and water rinses to remove both 4-fluorobenzoic acid and PPA, respectively. The crude product was recrystallized twice from either NMP or DMAC to afford a light brown crystalline powder. Prior to polymerization, the monomer was heated under vacuum at 210 °C for 4 h to remove water.

Scheme 2



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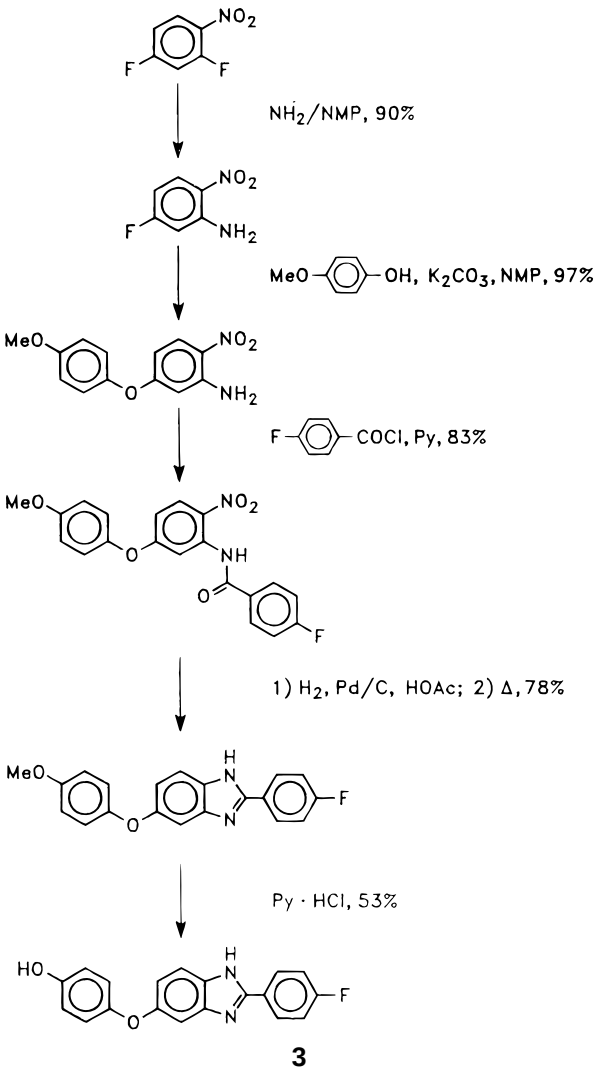
The synthesis of the requisite AB monomers (**2** and **3**) is interesting in its own right in that multiple aromatic nucleophilic substitution reactions are employed (Schemes 2 and 3). For the benzimidazole series, additional at the 2-position of 2,4-difluoronitrobenzene can be easily controlled to produce only the ortho monoadduct with high regiospecificity and yield. In the case of reaction of 2,4-difluoronitrobenzene with aniline, the monoadduct arising from selective reaction at the ortho position is isolated in excellent yield. The remaining fluorine at the para position is next substituted by a monoprotected hydroquinone (in this case, 4-methoxyphenol was utilized). With the benzene ring now fully functionalized, the 2-substituted imidazole ring is

Scheme 3



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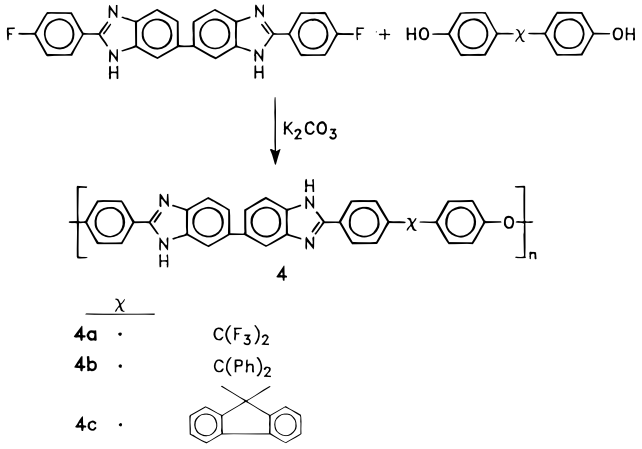
constructed next; in a one-pot reaction, the nitro group is first reduced by catalytic hydrogenation and then immediately converted to its 4-fluorobenzamide derivative. The resulting *o*-aminophenylbenzamide is isolated and then closed to the imidazole ring by simply boiling in acetic acid. With the fully substituted benzimidazole prepared, the only remaining task is to deprotect the methyl ether, and this is readily accomplished by simply heating the methyl ether precursor in pyridine hydrochloride to afford the final AB monomer. The overall yield for this five-step process is about 20%.

Nucleophilic aromatic substitution polymerizations are typically performed in a high-boiling aprotic polar solvent with the difluoride monomer being reacted with a bisphenol in the presence of a base, potassium carbonate, at elevated temperatures (ca. 180 °C). The potassium carbonate was used to convert the bisphenol into the more reactive anion. Since K_2CO_3 is a weak base, no hydrolytic side reactions with the bis(fluorophenyl)benzimidazoles are observed. Aprotic dipolar solvents are used in these poly(aryl ether) syntheses, since they effectively dissolve the monomers and solvate the polar intermediates formed. It is also important that these solvents solvate the polymer formed. In this study, we have investigated two solvent systems: an NMP/CHP (50/50) mixture and DMPU. NMP and CHP allow high reaction temperatures, 200 and 260 °C, respectively, and these high temperatures are required to maintain solubility of rigid or stiff-chain poly(aryl ethers). Although NMP alone tends to be a better solvent and is easier to handle, NMP/CHP solvent mixtures are often used since CHP is immiscible with water at temperatures above 100 °C. Thus, nonpolar cosolvents are not required to azeotrope the water generated during the polymerization. Alternatively, DMPU has been shown to be an excellent solvent for polyether syntheses, particularly for those polymers which are only marginally soluble in other dipolar aprotic solvents.[15] Furthermore, DMPU allows higher reaction temperatures (260 °C). We have observed that DMPU, when used in conjunction with toluene as a dehydrating agent, accelerates many nucleophilic substitution reactions. The increased activity of DMPU is probably due to its effectiveness in solvating the polar reagents and intermediates.

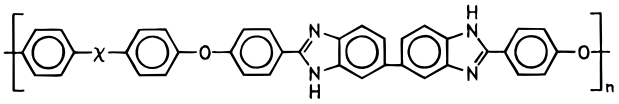
Scheme 4

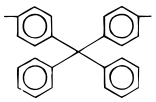


Polymerization of the benzimidazole with various bisphenols was carried out either in an NMP/CHP solvent mixture or in DMPU containing potassium carbonate (Scheme 4). The solids compositions were maintained at 20%, which is typical for most poly(aryl ether) syntheses, thereby avoiding side reactions with the fluoride ion. Irrespective of the polymerization solvent(s), toluene was used during the initial stages of the polymerizations to remove water generated by phenoxide formation as a toluene azeotrope. The solvent mixtures gave a reflux temperature between 150 and 165 °C. In an effort to keep the mixture anhydrous, the toluene was periodically removed through the Dean−Stark trap and replaced with more deoxygenated dry toluene. After bisphenoxide formation and dehydration, the polymerization mixtures were heated to 180−190 °C to effect the displacement reaction. In each case, high molecular weight polymer was attained within 48 h as judged by the dramatic increase in viscosity. The polymers were isolated in excess methanol and boiled in water to remove any remaining salts.

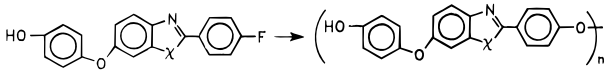
This general polymerization procedure was applied to a number of bisphenols affording poly(aryl ether benzimidazoles) **4a**−**c** (Scheme 4). The resulting polymers showed high T_g's (Table 1), consistent with the values of other heterocyclic-containing poly(aryl ethers). However, these values are somewhat lower than the poly(aryl ether benzimidazoles) reported by Connell et al. The viscosity values for the polymers ranged from 0.36 to 0.46 dL/g, respectively, and are considered moderate for a poly(aryl ether) synthesis. Irrespective of the polymerization temperature or solvent system surveyed (DMPU or CHP/NMP), there was minimal difference in molecular weight, as judged by the viscos-

Table 1. Characteristics of Poly(aryl ether benzimidazoles)



Sample Entry	χ	Solvent System	Tg, °C	$[\eta]^{25°C}_{NMP}$ dL/g
4a	$C(CF_3)_2$	DMPU	218	0.45
		NMP/CHP		0.46
4b	$C(Ph)_2$	DMPU	228	0.36
		NMP/CHP		0.44
4c		DMPU	250	0.43
		NMP/CHP		0.44

Scheme 5



5

χ	$[\eta]^{25°C}_{NMP}$ dL/g
5a NPh	0.45
5b NH	0.60

ity measurements. Solutions of the poly(aryl ether benzimidazoles) were cast from NMP to form films. However, the resulting films were somewhat brittle, consistent with moderate viscosity values. Presumably, the difficulty in obtaining higher molecular weight polymer results from the water absorption, offsetting the stoichiometry. Although the monomer was heated to 210 °C prior to polymerization, upon weighing and delivery, water absorption was observed.

The self-polymerization of the AB monomers (**2** and **3**) was carried out in a DMPU/toluene solvent mixture containing K_2CO_3 (Scheme 5). Stringent monomer delivery criteria, typical of most step-growth polymerizations to maintain the correct stoichiometry, were not required in the self-polymerization of the AB monomers, since 1:1 stoichiometry is inherent to the monomers. The solids composition was maintained between 20 and 25 wt %, analogous to conventional poly(aryl ether) synthesis. The weak base K_2CO_3 was used to form the phenoxide since hydrolytic side reactions with the activated halide are precluded. The water generated by phenoxide formation in the initial stages of the polymerization was removed as the toluene azeotrope. The reaction mixture was observed to reflux at the desired rate when the temperature of the oil bath was maintained between 150 and 160 °C. Toluene was periodically removed through the Dean−Stark trap and replaced with fresh deoxygenated toluene. Upon dehydration, the polymerization temperature was increased to 180−190 °C to effect the nucleophilic aromatic displacement reaction. High molecular weight polymer was obtained as judged by the dramatic increase in viscosity (24 h) (polymers **5a** and **5b**). The resulting polymer was filtered (to remove inorganic salts), coagulated in excess methanol, washed with boiling water (to remove remaining salts), and dried in a vacuum oven (80 °C) to a constant weight.

Each of the AB monomers were polymerized by this procedure. For the case of the phenylbenzimidazole-containing monomers, long reaction times were required to achieve high viscosity (i.e., 48 h at 180 °C). Attempts to reduce the polymerization time by increasing the temperature (240 °C) often resulted in the formation of gel. Conversely, the imidazole-containing AB monomer yielded high polymer in less than 24 h at 190 °C in DMPU. Interestingly, the shorter reaction times of benzimidazole-containing monomers in nucleophilic aromatic substitution polymerizations were also observed by Connell et al. In each of the above polymerizations, the subsequent polymers remained soluble during the course of the reaction, in spite of their rigid structures, allowing the formation of high molecular weight polymers. These results are consistent with those reported by Harris and co-workers on similar structures.

Table 2. Characteristics of Poly(aryl ether benzimidazoles) Prepared from AB Monomers

polymer	$[\eta]^{25°C}_{NMP}$ (dL/g)	T_g (°C)	polymer decomp temp (°C)	isothermal aging wt loss/*n* 300 °C	350 °C
5a	0.45	240	480	0.006	0.084
5b	0.58		470	0.120	0.100

A major concern with the self-polymerization of such AB monomers was the possibility of quantitative phenoxide formation prior to the displacement. For such an event, the resonance stabilization of the resulting anion could impede the electron-withdrawing ability of the benzimidazole and preclude polymerization. However, as proposed by Labadie et al., it is possible that an equilibrium exists between KCO_3 and $KHCO_3$ as well as the phenoxide and free phenol, and so it is likely that the initial fluoro displacement will occur at the phenolic monomers. However, it is noteworthy to point out that these AB monomers took substantially longer to polymerize than their benzoxazole and benzothiazole analogs, which may have resulted, to some extent, from possible bridging effects.

Summary

A new class of poly(aryl ether benzimidazoles) have been prepared by heterocyclic-activated displacement polymerization. In these reactions, the aryl ether linkages are generated in the polymer-forming reaction. We have demonstrated that the benzimidazole heterocyclic unit is sufficiently electron withdrawing to activate aryl fluorides toward nucleophilic displacement by a variety of nucleophiles. The appropriate substituted benzimidazole monomer was prepared and subjected to the displacement polymerization with various bisphenols in the presence of potassium carbonate in an NMP/CHP solvent mixture or in DMPU. Moderately high molecular weight polymer was readily achieved, and structural variety could be introduced through the use of different bisphenols. The resulting polymer showed T_g's in the 218−250 °C range, depending on the monomers used in the synthesis. This represents another example of the synthesis of poly(aryl ethers) based on a heterocyclic activated halo displacement, and this synthesis can be considered the benzimidazole analogue to the poly(ether imide) synthesis. Moreover, the heterocyclic-activated nucleophilic displacement chemistry provides a general methodology to high-temperature, high T_g poly(aryl ethers).

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