

Synthesis of Poly(phenylene oxide) and Poly(phenylene sulfide) Bilaterally Substituted with a Rigid Benzoxazole Group

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ABSTRACT: A study was done on the synthesis of a new poly(arylene ether) and poly(arylene sulfide) with rigid benzoxazole pendants using nucleophilic aromatic substitution reaction. 1,4-Bis(2-benzoxazolyl)-2,5-dibromobenzene (I) was synthesized in two steps starting from 2,5-dibromo-*p*-xylene. A model reaction of aryl dibromide (I) with two equivalent of thiophenol or *m*-cresol in a typical ether condensation and Ullmann ether reaction condition, respectively, gave very high yield (>93%) of substitution product, suggesting the feasibility of polymer formation in these systems. Monomer (I) was polymerized with 4,4'-thiobisbenzenethiol in 1-methyl-2-pyrrolidone (NMP) using NaOH or K₂CO₃ as base. Also the same monomer was polymerized with 4,4'-dihydroxydiphenyl ether in an Ullmann ether reaction. The molecular weight of the resulting polymers, however, seemed relatively low according to solution viscosity ($\eta_{inh} = 0.1-0.14$ dL g⁻¹). The benzoxazole-substituted poly(phenylene sulfide) polymer was only soluble in strong acids like sulfuric acid and trifluoroacetic acid. The poly(phenylene oxide) analog was soluble in several common organic solvents including chloroform, pyridine and *N,N'*-dimethylformamide. The polymers were stable up to 450°C as determined by the temperature that weight loss began to appear on TGA. Finally preliminary results on the photoluminescence property in solution were presented.

KEY WORDS Poly(arylene sulfide) / Poly(arylene ether) / Benzoxazole / Nucleophilic Aromatic Substitution / Ullmann Condensation /

A large number of poly(aryl ether)s and poly(aryl sulfide)s has been reported and studied during the past few decades as heat resistant, high performance polymers.¹⁻⁴ Also it is well known that poly(benzoxazole)s and poly(benzothiazole)s are among the most thermally stable polymers containing highly rigid heterocycles in the backbone. The most efficient means of introducing an aryl ether linkage in aromatic polymer system is through poly(aryl ether) synthesis, which involves the nucleophilic displacement of activated aromatic dihalides by alkali metal bisphenoxides in a polar aprotic medium. Other methods of poly(aryl ether) synthesis include oxidative coupling, Ullmann ether synthesis, and so on. As an activating group of the dihalide monomer, a variety of functionality has been employed so far, including sulfone, ketone, many different heterocycles, fluoro alkyl, etc. The activating group not only serves as electron withdrawing group but also stabilizes the negative charge developed through the formation of a Meisenheimer complex. Heterocycles such as oxadiazole, triazoles, and benzazoles serve as activating groups. In our previous report,⁵ a new aryl dibromide monomer with two benzoxazole (BOX) pendants, 1,4-bis(2-benzoxazolyl)-2,5-dibromobenzene [BOBr], was synthesized, and the polymerization reaction was studied. The BOBr monomer did not exhibit high enough reactivity toward phenolate (ArO⁻), presumably resulting from the lower reactivity of bromide compared to corresponding chloride or fluoride in a typical nucleophilic aromatic substitution ('NAS') reaction. The same monomer did show sufficiently high reactivity in an Ullmann condensation reaction catalyzed by CuCl-pyridine, where the ease of halogen displacement has been known to be the reverse of that observed in the usual activated halide systems, i. e.,

$I \sim \text{Br} > \text{Cl} \gg \text{F}$.¹ The wholly aromatic poly(aryl ether)s with rigid BOX pendant were prepared under this Ullmann reaction condition, and the polymer exhibited excellent thermal stability, relatively high glass transition temperatures, and enhanced solubility in many organic solvents.

As an attacking nucleophile, thiophenoxide (ArS⁻) is much stronger than phenoxide (ArO⁻) in terms of nucleophilicity for the aromatic substitution reaction.⁶ Though the BOBr monomer was not reactive enough for the clean displacement reaction with phenoxide under usual 'NAS' reaction condition, thiophenoxide, as a much stronger nucleophile, should exhibit enhanced reactivity for this system. This article discusses the reactivity and model reactions with the BOX-substituted aryl dibromide monomer, and the subsequent preparation of novel poly(arylene sulfide) from difunctional bis-thiophenol monomer. As a comparative and extending results of our previous work, the model reaction of BOBr monomer with *m*-cresol and polymerization reaction of BOBr monomer with 4,4'-dihydroxydiphenyl ether in a typical Ullmann condensation reaction condition are included in the present paper.

EXPERIMENTAL

All materials and solvents were purchased in highest purity available and used as-received unless otherwise indicated. 1-Methyl-2-pyrrolidinone (NMP), 1-cyclohexyl-2-pyrrolidinone (CHP) and toluene were dried over CaH₂ and distilled before use. 4,4'-Thiobisbenzenethiol and 4,4'-dihydroxydiphenyl ether were purified by recrystallization and sublimation.

IR spectra were obtained on a Unicam 1000 FT-IR spectrometer. NMR spectra were taken on a Varian Unity Inova 500 MHz Spectrometer at room tempera-

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ture. Thermal analysis (DSC/TGA) was carried out on a Perkin Elmer 7 Series thermal analysis system. Mass spectra (MS) were obtained on a Kratos Concept-S (double-focusing type) spectrometer. Solution viscosity was measured by Ubbelohde (type OB) capillary viscometer using H₂SO₄ as the solvent. Fluorescence measurements were made with a Aminco-Bowman spectrophoto fluorimeter at 25°C.

1,4-Bis(2-benzoxazolyl)-2,5-dibromobenzene [BOBr] (I) was synthesized with high yield by well-known polyphosphoric acid (PPA) catalyzed condensation reaction between 2-aminophenol and 2,5-dibromoterephthalic acid prepared by oxidation of 2,5-dibromo-*p*-xylene. mp (DSC): 292°C; IR (KBr pellet): 3088, 1609 (oxazole), 1449, 1374, 1243, 1100, 1031 (Ar-Br), 807, 751 cm⁻¹; ¹H NMR (trifluoroacetic acid-*d*): 8.29 (2H, s), 7.55 (4H, dd), 7.39 (4H, tt) ppm; ¹³C NMR (trifluoroacetic acid-*d*): 151.5, 140.5, 132.8, 131.5, 131.2, 130.0, 123.8, 118.4, 114.3 ppm; MS (EI): 470 (M⁺)

1,4-Bis(2-benzoxazolyl)-2,5-bis(3-methylphenoxy)benzene (Model compound, II) was prepared by a CuCl-catalyzed Ullmann ether synthesis from BOBr (I) and *m*-cresol as reported previously. Yield after column chromatography: 93%; mp. (DSC): 276°C; IR (KBr pellet): 3051, 1598, 1544, 1463, 1413, 1250 (Ar-O-Ar), 1196, 752 cm⁻¹; ¹H NMR (trifluoroacetic acid-*d*): 7.61(2H, *d*), 7.41 (8H, *m*), 7.07 (2H, *t*), 6.91 (2H, *d*), 6.67 (4H, *t*), 2.02 (6H, *s*) ppm; ¹³C NMR (trifluoroacetic acid-*d*): 160.9, 156.7, 154.7, 151.1, 145.5, 133.5, 133.3, 132.1, 131.6, 130.4, 123.5, 119.8, 119.7, 118.2, 118.1, 114.9, 22 ppm; MS (EI): 524 (M⁺)

The same model reaction was attempted in a typical NAS reaction conditions using NMP and K₂CO₃ as the solvent and the base, the reaction product was found to a complicated mixture, so that separation of desired disubstituted model compound was difficult.

1,4-Bis(2-benzoxazolyl)-2,5-bis(thiophenoxy)benzene (Model Compound, III) was prepared by typical aryl ether synthesis from BOBr (I) and thiophenol. In a 3-neck reaction flask equipped with a nitrogen inlet and Dean-Stark trap fitted with a condenser and a nitrogen outlet, 0.454 g (11.35 mmol) of NaOH in 1.5 mL of water and 1.227 g (11.35 mmol) of *m*-cresol in a mixture of NMP (15 mL) and toluene (10 mL, 3 times) were kept with stirring and the temperature was increased to 150°C to remove water of *m*-cresolate formation *via* an azeotrope with toluene. After 4–6 h, the system was dehydrated and the reaction was cooled to room temperature. BOBr (I) (2.425 g, 5.158 mmol) was added and stirred for 18 h at 180°C. The reaction mixture was precipitated into 200 mL water and the aqueous solution was acidified by addition of 1 N-HCl. The yellow precipitate was filtered, washed and dried in vacuum at 90°C for 24 h. Above crude product was flash column chromatographed (CH₂Cl₂, silica gel) to remove impurities and then recrystallized from *N,N'*-dimethylformamide (DMF) to obtain a light-yellow crystalline product (yield after column chromatography: 93%). mp(DSC): 285°C; IR (KBr): 3050, 1554, 1454, 1244, 1038, 745, 691 cm⁻¹; ¹H NMR (trifluoroacetic acid-*d*): 8.24 (2H, *s*), 8.0 and 7.94 (each 2H, *d*), 7.9 (4H, *m*), 7.4–7.6 (10H, *m*) ppm; ¹³C NMR (trifluoroacetic acid-*d*): 162.2, 150.5, 142.4, 136.0, 134.5, 132.1, 131.8, 131.1, 129.9, 129.4, 125.5,

117.2, 113.9 ppm; MS (EI): 529 (M⁺)

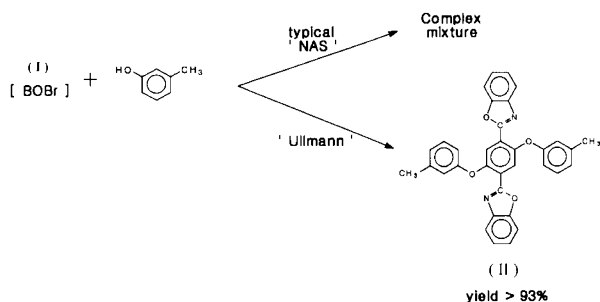
Synthesis of Poly(aryl ether) (IV) by CuCl-Catalyzed Ullmann Condensation Reaction. In a 3-neck reaction flask equipped with a nitrogen inlet and Dean-Stark trap fitted with a condenser and nitrogen outlet, 4,4'-dihydroxydiphenyl ether (0.430 g, 2.127 mmol) was dissolved in 30 mL NMP, and then K₂CO₃ (0.441 g, 3.190 mmol) was added under N₂ purge. To the solution were added 20 mL toluene portionwise at the bath temperature of 150°C to remove water of bisphenolate formation *via* an azeotrope with toluene. After 4–6 h, the system was dehydrated completely and the reaction was cooled to 80°C. BOBr monomer (I) (1 g, 2.127 mmol), and CuCl (0.027 g) in 20 mL pyridine were added subsequently and stirred for 18 h at reflux. After reaction the reaction mixture was precipitated into 300 mL aq-HCl. The precipitate was filtered, washed and dried in vacuum at 90°C for 12 h. The product was dissolved in 25 mL CHCl₃ and reprecipitated into methanol, which was filtered, washed and dried in vacuum. (yield 85%) IR(KBr): 3055, 2965, 1560, 1489, 1227 (Ar-O-Ar), 749 cm⁻¹; ¹H NMR (CDCl₃): 6.5–7.6 (aromatic protons, 18 H), 1.65 (CH₃, 6H) ppm.

Synthesis of Poly(aryl sulfide) (V) by Nucleophilic Aromatic Substitution Reaction. In a 3-neck reaction flask equipped with a nitrogen inlet and a Dean-Stark trap fitted with a condenser and nitrogen outlet, 4,4'-thiobisbenzenethiol (0.4856 g, 2.127 mmol) was dissolved in 30 mL of NMP and K₂CO₃ (0.441 g, 3.190 mmol) was added under N₂ purge. To this solution was added 20 mL toluene portionwise at the bath temperature of 150°C to remove water of bithiophenolate formation *via* an azeotrope with toluene. After 4–6 h, the system was dehydrated completely and the reaction was cooled to 80°C. BOBr monomer (I) (1 g, 2.127 mmol) was added and stirred for 20 h at 180–190°C under argon flow. The reaction mixture was precipitated into 300 mL aq-HCl. The light-brown precipitate was filtered, washed with water and toluene repeatedly, then dried in vacuum at 90°C for 24 h (yield 83%). IR (KBr): 3060, 1612, 1564, 1473, 1450, 1231, 1040, 801, 746 cm⁻¹; ¹H NMR (trifluoroacetic acid-*d*): 7.5–8.0 (aromatic protons, br) ppm

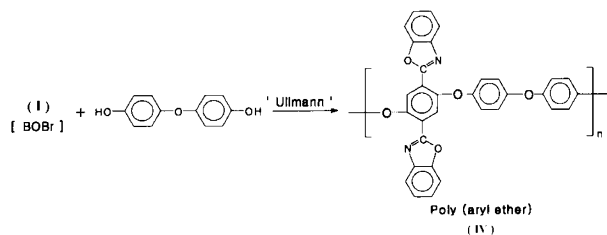
RESULTS AND DISCUSSION

1,4-Bis(2-benzoxazolyl)-2,5-dibromobenzene (BOBr, I) was prepared, as previously reported, by PPA-catalyzed condensation reaction between 2-aminophenol and 2,5-dibromoterephthalic acid obtained by KMnO₄ oxidation of 2,5-dibromo-*p*-xylene. From the model reaction with *m*-cresol, the dibromide monomer was proved not to possess enough reactivity for typical aromatic displacement reaction between activated aryl halide and phenolate, possibly due to the relatively lower reactivity of bromide compared to corresponding chloride or fluoride, as the general reactivity order is F ≫ Cl > Br.

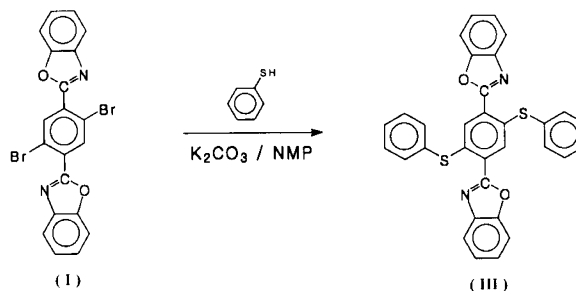
Ullmann condensation reaction is another method to form an aryl ether, where Cu(I) salts are used as reactive catalysts. The ease of halogen displacement is the reverse of that observed in usual activated halide system, i. e., I ~ Br > Cl ≫ F. When the BOBr monomer was reacted with *m*-cresol in Ullmann ether reaction condition,



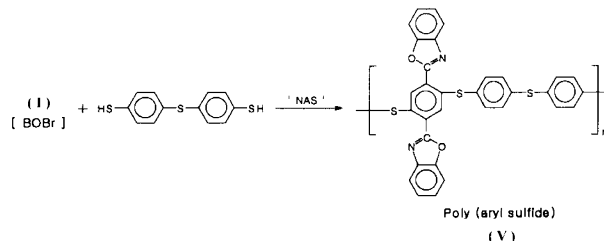
Scheme 1.



Scheme 2.



Scheme 3.



Scheme 4.

substitution occurred almost quantitatively, suggesting the feasibility of polymer formation in this system (Scheme 1). As a representative example, BOBr monomer was polymerized with 4,4'-dihydroxydiphenyl ether to give the corresponding polymer, benzoxazole-substituted poly(phenylene oxide), as the reaction scheme was shown above (Scheme 2). The polymer possessed inherent viscosity of 0.14 dL g^{-1} at 25°C in chloroform, and T_g of 211°C was observed from DSC. Also the polymer was soluble in many common organic solvents including chloroform, pyridine, DMF and was stable to *ca.* 450°C under nitrogen (See Figure 3).

Thiophenoxide (ArS^-) is much stronger than phenoxide (ArO^-) in terms of nucleophilicity for the usual nucleophilic aromatic substitution reaction of activated aryl halide.⁶ So, it was worthwhile to try thiophenoxide reagent, as a much stronger nucleophile, where the enhanced reactivity for halide displacement is expected for the same monomer.

The model reaction of monomer (I) with thiophenol under usual 'NAS' reaction conditions using a base, K_2CO_3 , in NMP was carried out under argon atmosphere (Scheme 3). The substitution reaction seemed quite clean to give the desired disubstituted product (model compound) with high yield over 93%. The FT-IR and ^1H NMR spectra of model compound (III) are shown in Figures 1 and 2, respectively.

Characteristic oxazole absorption bands at 1620 and 1244 cm^{-1} , and aryl sulfide C-S-C absorption band at 810 cm^{-1} , respectively, were observed from FT-IR. ^1H NMR spectrum shows protons of the central ring at chemical shift of 8.24 (2H, *s*), protons of the benzo ring at 7.8 – 8.0 (8H, *m*), and aromatic protons of thiophenol at 7.4 – 7.5 (10H, *m*), respectively, with correct integration ratios. MS (EI) also exhibited molecular ion mass (M^+) of 529 Da , coincident with the calculated value, due to the enhanced reactivity of thiophenolate for the nucleophilic displacement reaction of aryl dibromide monomer (I), compared with the lower reactivity of phe-

nolate previously described. Also the clean model reaction with high yield suggests that the same reaction can be applied for the preparation of poly(arylene sulfide) according to the reaction scheme shown above (Scheme 4). A difunctional 4,4'-thiobisbenzenethiol monomer was used for polymerization with monomer (I).

The polymerization reaction was carried out under typical 'NAS' reaction conditions using K_2CO_3 and NMP as base and solvent, respectively. Even though the high reactivity of thiophenolate anion for the bromine displacement reaction was demonstrated from the previous model reaction, the resulting polymer seemed to possess relatively low molecular weight, which was estimated from its solution viscosity (0.11 dL g^{-1} in concentrated sulfuric acid). Most probably the solubility of this highly rigid aromatic polymer is responsible for this. To improve the molecular weight of the polymer, the polymerization reaction was attempted in NMP/CHP (50 : 50) mixture considering the moisture sensitivity of this reaction system. Also the polymerization was conducted in Ullmann condensation reaction condition using CuCl/Py at higher temperature. No appreciable improvement in the molecular weight of the resulting polymer, however, could be obtained, unfortunately.

The polymer was insoluble in most organic solvents. It showed solubility only in strong acids such as concentrated sulfuric acid and trifluoroacetic acid, and partial solubility in DMF, NMP and 1,2-dichlorobenzene. DSC did not show any thermal transitions up to 350°C . From the TGA (Figure 3), a decomposition onset was observed at the temperature of *ca.* 450°C .

The photophysical characterization of this conjugated aromatic system included measurement of absorption and emission spectra in solution. Figure 4 shows the absorption and emission spectra of monomer (I) and model compound (III) in DMF solution, and polymer (V) in 1,1,3,3-tetramethylurea solution, respectively. All compounds displayed strong blue fluorescence. Monomer (I) displayed a relatively broad absorption band with a

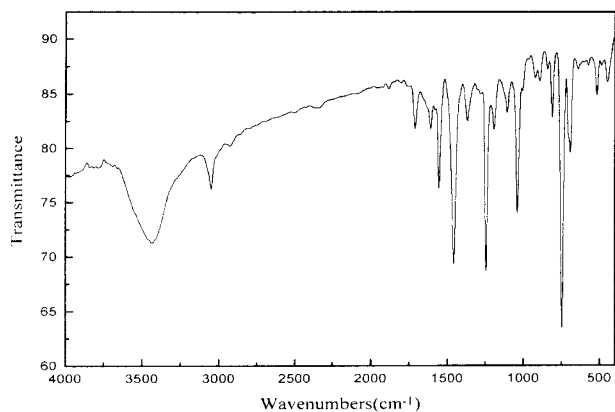


Figure 1. FT-IR spectrum of model compound (III).

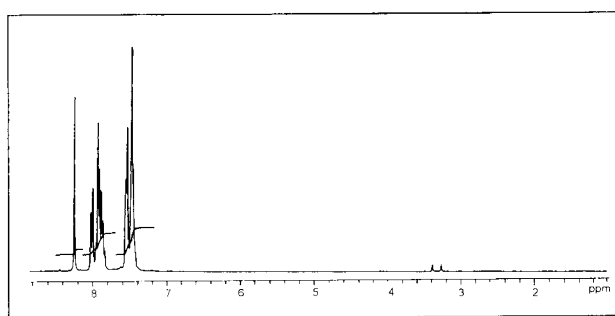


Figure 2. ¹H NMR spectrum of model compound (III).

maximum at 312 nm and the fluorescence spectrum showed an emission maximum at 412 nm when excited at the wavelength of absorption maximum. Model compound (III) and polymer displayed relatively sharp absorption bands with a maximum at around 290 nm with a shoulder and the fluorescence spectrum showed an emission maximum at 467 and 500 nm, respectively. Compared to the monomer, the emission bands of model compound and polymer were observed to be red-shifted with band broadening, probably caused by conjugation of thiophenyl group with the bis-benzoxazolyl benzene structure.

In conclusion, 1,4-bis(2-benzoxazolyl)-2,5-dibromobenzene (I) was synthesized in two step starting from 2,5-dibromo-*p*-xylene. Monomer (I) was not reactive enough with phenoxide in the usual nucleophilic aromatic substitution reaction condition. The same monomer was sufficiently reactive in an Ullmann ether reaction condition, which allowed preparation of the corresponding polymer with bisphenol monomers. A model reaction of monomer (I) with two equivalents of thiophenol provided very high yield of substitution product in a typical aromatic substitution reaction condition, suggesting not only enhanced reactivity of thiophenoxide as a much stronger nucleophile, but the feasibility of polymer formation in this system. Monomer (I) was polymerized with 4,4'-thiobisbenzenethiol in NMP using NaOH or K₂CO₃ as the base to give the benzoxazole-substituted poly(phen-

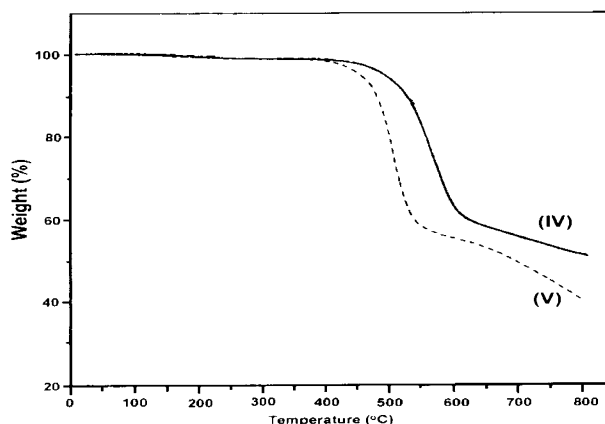


Figure 3. TGA thermograms of polymer (IV) and (V) in nitrogen.

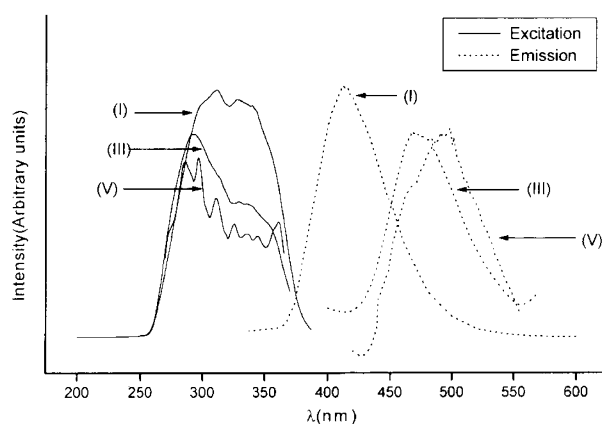


Figure 4. Absorption (—) and emission (---) spectra of monomer (I), model compound (III), and polymer (V).

ylene sulfide). The molecular weight of polymer, however, seemed relatively low according to the solution viscosity. From the fluorescence measurement, the prepared compounds were observed to exhibit strong blue photoluminescence in solution.

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