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Registry No. Ia (SRU), 111791-73-2; Ia (copolymer), 111791-46-9; Ib (SRU), 111791-74-3; Ib (copolymer), 111791-47-0; Ic (SRU), 111791-71-0; Ic (copolymer), 111791-44-7; Id (SRU), 111791-72-1; Id (copolymer), 111791-45-8; Ie (SRU), 126615-65-4; Ie (copolymer), 126615-61-0; H_2SO_4, 7664-93-9.

Poly(aryl ether-benzoxazoles)

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ABSTRACT: A general method for the preparation of poly(aryl ether-benzoxazoles) has been developed where the generation of an ether linkage is the polymer-forming reaction. We found that aryl fluorides para to a 2-benzoxazolyl group were activated toward nucleophilic aromatic substitution with phenoxides. Facile displacement occurred at this position since the benzoxazole 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). Appropriately substituted dihalo bisbenzoxazoles, 2,2′-bis[2-(4-fluorophenyl)benzoxazol-6-yl]hexafluoropropane, 2,2′-bis(4-fluorophenyl)-6,6′-bibenzoxazole, and 2,2′-(4-fluorophenyl)-5,5′-bibenzoxazole, were prepared and polymerized with bisphenols in *N*-methyl-2-pyrrolidone in the presence of K_2CO_3. High molecular weight polymers were obtained, with glass transition temperatures ranging from 213 to 300 °C. The resulting polymers were processable from solution or the melt and showed excellent thermal stability and mechanical properties. This synthetic route affords the poly(benzoxazole) analogue of poly(ether-imide) and shows many of the same desirable characteristics.

Introduction

Aromatic poly(benzoxazoles) (PBO) are a class of high-temperature heterocyclic polymers that show excellent thermal stability.[1-5] PBO's are generally prepared by step-growth polymerization of aromatic bis(*o*-aminophenols) with aromatic diacid derivatives.[1-5] The use of PBO's has been limited since they are soluble only in strong acids and cannot be processed from organic solvents. Recently, a novel synthetic route for the synthesis of PBO's was reported that involved the polymerization of silylated bis(*o*-aminophenols) with aromatic diacid chlorides.[6] Monomers containing flexible hexafluoroisopropylidene linkages afforded PBO's that were soluble in

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common organic solvents.

Alternatively, the introduction of ether linkages is known to improve the solubility characteristics of rigid-temperature polymers. An efficient means of introducing ether linkages in heterocyclic polymers is through a polyether synthesis, where the desired preformed heterocyclic ring is introduced in the bishalide (nitro) or bisphenol monomer. An important example of this approach is the synthesis of poly(ether–imide) via a nitro displacement polymerization of bis(nitrophthalimides) with bisphenols.[7] Poly(ether–imides) are engineering thermoplastics that have excellent solution and melt processability relative to rigid and semirigid polyimides. Hedrick et al. demonstrated the synthesis of poly(aryl ether–phenylquinoxalines) by polymerization of bis(fluorophenylquinoxalines) with bisphenols.[8] This polymerization was based on the activation of the fluoro group toward nucleophilic aromatic substitution by the pyrazine component of the quinoxaline heterocyclic. The resulting polymers could be processed from common organic solvents or the melt. Connel et al. polymerized bisphenols containing preformed quinoxaline[9] and imidazole[10] rings with conventional activated dihalides (e.g., 4,4′-difluorodiphenyl sulfone, 4,4′-difluorobenzophenone, etc.) to give processable heterocyclic containing poly(aryl ethers) that were amenable toward conventional thermoplastic composite fabrication.[9,10]

We felt that the heterocyclic activated poly(aryl ether) synthesis could be extended to other ring systems besides imides and phenylquinoxalines. In particular, we are interested in applying this approach to prepare more processable PBO's, poly(benzimidazoles) and poly(benzthiazoles). In this paper we will describe our investigation of oxazole-activated fluoro displacement as a route to PBO's containing aryl ether linkages, with the objective of extending the scope of the heterocyclic activated halo displacement as well as obtaining PBO's that may be processed from common organic solvents or the melt.

Experimental Section

Materials. *N*-Methyl-2-pyrrolidone (NMP) and *N*-cyclohexyl-2-pyrrolidone (CHP) were distilled from calcium hydride, and toluene and triethylamine were used without further purification. Aminophenols (Aldrich) were purified by sublimation. 4-*tert*-Butylphenol, *m*-cresol, 4-fluorobenzoic acid, and oxalyl chloride (Aldrich) were used without further purification. 2,2′-Bis(3-amino-4-hydroxyphenyl)hexafluoropropane (Central Glass Co. Inc.), 3,3′-dihydroxy-4,4′-diaminobiphenyl (Chriskev Co. Inc.), and 3,3′-diamino-4,4′-dihydroxybiphenyl (Chriskev Co. Inc.) were used as received.

4-Fluorobenzoyl chloride was prepared by the reaction of 4-fluorobenzoic acid (98 g, 0.70 mol) with oxalyl chloride (100 g, 0.79 mol) in 250 mL of chloroform. The reaction was stirred until a clear solution was obtained which usually took 24 h. The 4-fluorobenzoyl chloride was concentrated and purified by distillation (180 °C, N_2 atmosphere) to give 87 g of 4-fluorobenzoyl chloride as a clear liquid.

2-(4-Fluorophenyl)benzoxazole (1). 4-Fluorobenzoyl chloride (1.62 g, 10.3 mmol) was added dropwise to a solution of 2-aminophenol (1.12 g, 10.3 mmol) and triethylamine (1.04 g, 10.3 mmol) in 200 mL of dry THF at −42 °C (dry ice in acetonitrile bath) and then stirred for 6 h. The reaction mixture was added to 500 mL of water, and the product was isolated by filtration and dried under vacuum to give the intermediate amide. The amide was heated in a sublimator at 200 °C together with 4.6 g of 4-Å molecular sieves under nitrogen yielding 1.58 g of 1 (72% yield) as a light yellow crystalline solid: mp 101 °C; ^{1}H NMR ($CDCl_3$) δ 7.20–7.27 (m, 2 H), 7.37–7.41 (m, 2 H), 7.59–7.63 (m, 1 H), 7.78–7.82 (m, 1 H), 8.26–8.33 (m, 2 H). Anal. Calcd for $C_{13}H_8N_1O_1F_1$: C, 73.23; H, 3.75; N, 6.57. Found: C, 73.48; H, 3.77; N, 6.81.

2-[4-(3-Methylphenoxy)phenyl]benzoxazole (2). A three-neck 25-mL flask fitted with a Dean-Stark trap was charged with *m*-cresol (346 mg, 3.20 mmol), a 23.85 wt % aqueous sodium hydroxide solution (128 mg, 3.20 mmol), 5 mL of NMP, and 10 mL of toluene. The water was removed as a toluene azeotrope (150 °C), and the resulting sodium cresolate solution was cooled to room temperature and treated with 1 (640 mg, 3.00 mmol) in 2 mL of NMP. The reaction mixture was heated to 170 °C for 16 h, cooled, dissolved in ether, and washed 4× with water. The ether layer was dried ($MgSO_4$) and concentrated, and the resulting solid was purified by chromatography (5% ethyl acetate/hexane, silica gel) to afford 0.86 g of 2 (95%) as a white crystalline solid; mp 80–81 °C. Anal. Calcd for $C_{13}H_8NO$: C, 73.23; H, 3.83; N, 6.63. Found: C, 73.34; H, 3.64; N, 6.58.

2,2′-Bis[2-(4-fluorophenyl)benzoxazol-6-yl]hexafluoropropane (3). A three-neck 250-mL flask fitted with a Dean-Stark trap and condenser was charged with 2,2′-bis(3-amino-4-hydroxyphenyl)hexafluoropropane (50 g, 87 mmol), 4-fluorobenzoic acid (50 g, 357 mmol), and 120 mL of CHP. The reaction mixture was heated and stirred under a nitrogen blanket at 130 °C for 3 days and at 260 °C for 24 h. The nitrogen flow was then directed through the flask for 24 h at 260 °C to remove the remaining water and excess acid. The CHP was removed by vacuum distillation affording a viscous liquid. The product was precipitated by the addition of 300 mL of ether and recrystallized from methanol and a second time from toluene to give 45.7 g of 3 as a white crystalline solid (91% yield): mp 195–197 °C; ^{1}H NMR ($CDCl_3$) δ 7.11–7.26 (m, 4 H), 7.36 (d, 2 H), 7.52 (d, 2 H), 7.90 (s, 2 H), 8.17–8.25 (m, 4 H). Anal. Calcd for $C_{29}H_{14}N_2O_2F_8$: C, 60.63; H, 2.46; N, 4.88. Found: C, 60.42; H, 2.44; N, 4.89.

2,2′-Bis(4-fluorophenyl)-6,6′-bibenzoxazole (4). A 100-mL three-necked flask, equipped with a Dean-Stark trap and condenser was charged with 4,4′-diamino-3,3′-dihydroxybiphenyl (17 g, 77 mmol), 4-fluorobenzoic acid (23 g, 164 mmol), and 50 mL of CHP. The reaction was heated to 130 °C for 24 h and then 260 °C for 24 h. Initially, nitrogen flow was passed through the reaction for 2 h at 260 °C to remove the water generated and then switched to a positive pressure. 4-Fluorobenzoic acid (5 g) was added to the reaction and maintained at 260 °C for another 24 h. The product crystallized upon cooling and was isolated by filtration and rinsed with methanol (500 mL) to give 32 g (98% yield) of the crude product 4. Recrystallization from cyclohexanone gave a pale yellow powder, mp 279–281 °C. Anal. Calcd for $C_{26}H_{14}N_2O_2F_2$: C, 73.58; H, 3.32; N, 6.60. Found: C, 73.16, H, 3.35; N, 6.51.

2,2′-Bis(4-fluorophenyl)-5,5′-bibenzoxazole (5). Compound 5 was prepared analogous to 4 utilizing 3,3′-diamino-4,4′-dihydroxybiphenyl (21.8 g, 98 mmol), 4-fluorobenzoic acid (25.0 g, 178 mmol), and 100 mL of CHP. Upon completion, the reaction was diluted with 75 mL of NMP. The crude product crystallized upon cooling to give 39 g of crude product (93% yield). Recrystallization from cyclohexanone afforded 5 as pale beige crystalline needles, mp 294–297 °C. Anal. Calcd for $C_{26}H_{14}N_2O_2F_2$: C, 73.58; H, 3.32; N, 6.60. Found: C, 73.25, H, 3.38; N, 6.46.

2-[4-(4-*tert*-Butylphenoxy)phenyl]benzoxazole (6) and Ether Interchange. A 25-mL three necked flask fitted with a Dean-Stark trap was charged with 1 (0.9583 g 4.491 mmol), 4-*tert*-butylphenol (0.6747 g, 4.491 mmol), K_2CO_3 (0.93 g, 6.7 mmol), and 5 mL of CHP. The reaction was heated to 140 °C under a nitrogen flow for 6 h and then another 20 h at 180 °C to effect the displacement reaction affording 2-[4-(4-*tert*-butylphenoxy)phenyl]benzoxazole. *m*-Cresol (0.146 g, 1.346 mmol) was added, and aliquots were taken out periodically during the 16-h of reaction time, partitioned between methylene chloride and 5% acetic acid, and analyzed by GC (70–270 °C, 5 °C/min).

Bisphenols (7). 4,4′-(Hexafluoroisopropylidene)diphenol (**7a**) (Aldrich) and bis(4-hydroxyphenyl)diphenyl methane (**7b**) (Applied Organic Silicone) were each recrystallized twice from toluene. 9,9′-Bis(hydroxyphenyl)fluorene (**7c**) was kindly supplied by P. M. Hergenrother (NASA Langley) and used as received.

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–benzoxazole) based on **3** and **7a** is provided. The flask was charged with **3** (3.4707 g, 6.0420 mmol) and **7a** (2.0314 g, 6.0420 mmol) and carefully washed in the flask with 25 mL of NMP. 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 140 and 150 °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 140 °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 dark 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 **8a** 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 in a vacuum oven (80 °C) to a constant weight. In each case the yield was essentially quantitative.

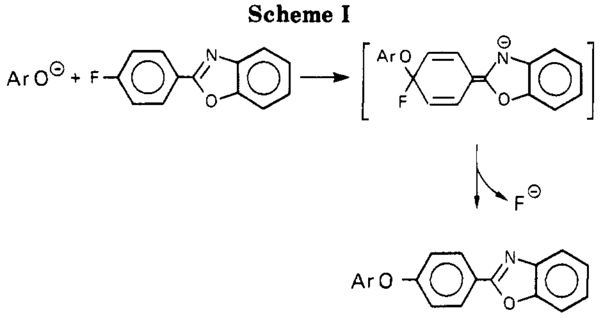
Characterization. Glass transition temperatures, taken as the midpoint of the change in slope of the base line, were measured on a Du Pont DSC 1090 instrument with a heating rate of 10 °C/min. Films for thermal analysis were cast from NMP and heated to 325 °C (5 °C/min heating rate) and held for 30 min. 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). Mechanical property measurements on thin solution cast films were made on an Instron tensile tester at a strain rate of 10 mm/min. Dynamic mechanic measurements were made on a Polymer Laboratories dynamic mechanical thermal analyser (DMTA) in the tension mode with a heating rate of 10 °C/min (10 Hz). Environmental stressed cracking measurements were made on a Polymer Laboratories tensile tester. Samples were stressed to approximately 40 MPa and exposed to different chemical environments for 5 min, and the stress was remeasured.

Results and Discussion

The synthesis of poly(aryl ethers) is based on the nucleophilic aromatic displacement of an aryl halide with a phenoxide in polar aprotic solvents, where the aryl halide is activated by an electron-withdrawing group (e.g., carbonyl or sulfone).[11,12] These activating groups can also accept a negative charge lowering the activation energy for the displacement through a Meisenheimer complex. Recently, a novel heterocyclic activated halo displacement from the 6- or 7-positions of a quinoxaline ring system with a phenoxide was reported and used to synthesize high molecular weight poly(aryl ether–phenylquinoxalines).[8]

It seemed plausible that other heterocyclic ring systems, such as benzoxazoles, could activate the nucleophilic aromatic substitution of aryl halides by phenoxides. The rationale for facile nucleophilic aromatic substitution from a benzoxazole-substituted benzene ring was 2-fold: (1) The electron-poor oxazole ring would have the effect of an electron-withdrawing group. (2) A Meisenheimer complex would form as a stabilized intermediate (and/or transition state) during the transformation due to resonance of the negative charge into the oxazole ring (Scheme I).

Scheme I



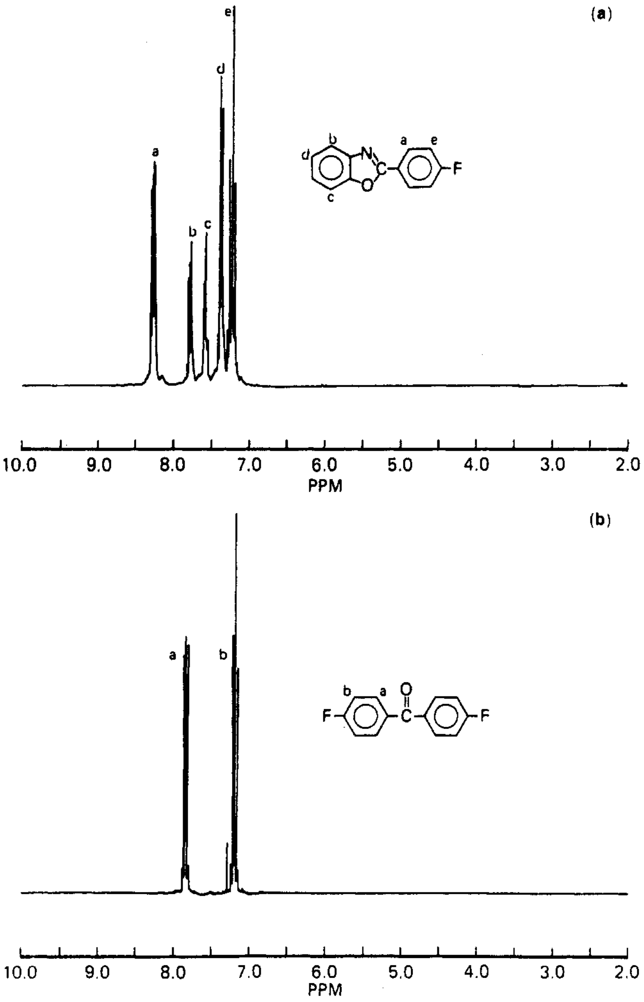
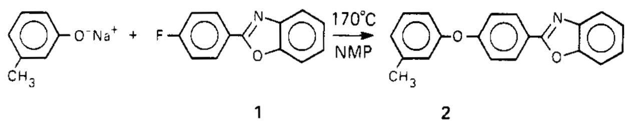


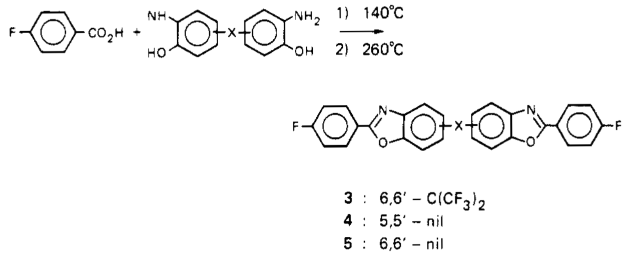
Figure 1. ^{1}H NMR spectra of (a) 2-(4-fluorophenyl)benzoxazole and (b) 4,4′-difluorobenzophenone.

The electronic effect of oxazole ring on both the benzo aromatic ring and the 2-phenyl group can be evaluated by ^{1}H NMR, as the deshielding of the protons ortho to a substituent is indicative of an electron-withdrawing group (Figure 1). The ^{1}H NMR spectral assignments for **1** show the ortho protons of the 2-phenyl ring (H_a) are at δ 8.3, further downfield than the ortho protons of benzo ring, H_b and H_c, at δ 7.8 and 7.6, respectively. This indicates the oxazole has a greater electron-withdrawing effect on the 2-phenyl group than the benzo ring of the benzoxazole. Conversely, a pyrazine ring in phenylquinoxalines was found to have greater effect on the benzo ring.[8] Comparison of the assignments of **1** with 4,4′-difluorobenzophenone shows the protons ortho to the benzoxazole (H_a) have a chemical shift of δ 8.3, as compared to δ 7.9 for the protons ortho to the ketone in 4,4′-difluoroben-

Scheme II



Scheme III



zophenone (Figure 1). This demonstrates the electron-withdrawing effect of the 2-benzoxazolyl group on a benzene ring in the ground state is comparable to a ketone and portends the likelihood of facile nucleophilic aromatic substitution at the para position of the 2-phenyl ring.

To demonstrate the feasibility of the benzoxazole-activated aryl ether synthesis, the reaction of sodium cresolate with 1 was investigated (Scheme II). An anhydrous solution of sodium cresolate in NMP was reacted with 1 at room temperature and then heated to 170 °C. After 1 h, HPLC analysis showed quantitative conversion of 1 had occurred with the formation of a single product peak. The expected benzoxazole substituted ether 2 was isolated as a single homogeneous product in high yield (95%) after flash chromatography. The model reaction demonstrated that the fluoride para to the benzoxazole group was cleanly displaced by phenoxides and that this transformation is a suitable as a polymer-forming reaction.

The synthesis of poly(aryl ether–benzoxazoles) required preparation of various bis(fluorophenyl)bibenzoxazoles (**3–5**). The synthesis of **3–5** involved the reaction of 4-fluorobenzoic acid with various bis(aminophenols) in CHP at 260 °C (Scheme III). Initially, the reactions were maintained at 140 °C (48–72 h) to form the amide. Since CHP is not miscible with water at elevated temperatures (80–100 °C), the water generated upon amide formation was efficiently removed through the Dean-Stark trap allowing the amide reaction to go to completion. In these early stages of the reactions, higher temperatures could not be employed since the 4-fluorobenzoic acid readily sublimed above 160 °C. Upon dehydration and amide formation (24 h), the reactions were slowly heated to 260 °C to effect the ring closure and benzoxazole formation. In each case, quantitative conversion of the bis(aminophenol) was observed (HPLC) with the formation of a single product peak and no evidence of side reactions. The excess acid sublimed from the reaction mixtures at these temperatures leaving only the product, which after recrystallization afforded polymer grade monomers **3–5**.

The synthesis of the difluorobibenzoxazoles could also be prepared in polyphosphoric acid which is the solvent of choice for preparing rigid PBOs and other structures.[13] Compound 1 was readily synthesized by the reaction of 2-aminophenol with an excess of 4-fluorobenzoic acid in polyphosphoric acid (30% solids) at 165 °C. However, the crude product was difficult to isolate and purify from the acid leading to poor yields. Likewise, similar problems were encountered in the preparation of **3–5** in polyphosphoric acid, and the CHP route was considered the best method.

The synthesis of poly(aryl ethers) is generally carried out in aprotic dipolar solvents such as NMP, CHP, or dimethyl sulfoxide (DMSO). These solvents effectively solvate the monomers, polar intermediates, and in most cases the subsequent polymer. Furthermore, the formation of the Meisenheimer complex is strongly influenced by the solvent, and polar solvents stabilize this complex assisting the displacement reaction. The choice of the solvent depends on the solubility of the polymer and the polymerization temperatures required for achieving high molecular weight. NMP and CHP allow the highest reaction temperatures, 200 and 260 °C, respectively, and these high polymerization temperatures are required in the preparation of rigid or stiff chain poly(aryl ethers) to maintain solubility. Furthermore, since CHP is not miscible with water at temperatures above 100 °C, nonpolar cosolvents used to azeotrope the water generated during the polymerization are not required.

Polymerization of **3** and **4** with various bisphenols was carried out in an NMP/toluene (2/1) solvent mixture in the presence of K_2CO_3 (Scheme IV).[14] The K_2CO_3 was used to convert the bisphenol into the more reactive bisphenoxide, and since K_2CO_3 is a weak base, no hydrolytic side reactions with the difluorobibenzoxazoles were observed. As in the case for the most polyether synthesis, the solids composition was maintained between 20 and 25 wt %. The water generated by bisphenoxide formation in the initial stages of the polymerization was removed as an azeotrope with toluene. This solvent mixture gave a reflux temperature between 140 and 150 °C. In an effort to maintain a dry system the toluene was periodically removed through the Dean-Stark trap and replaced with deoxygenated dry toluene. Upon completion of 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 24 h as judged by the dramatic increase in viscosity. The polymers were isolated in a 10× excess of methanol and boiled in water to remove the remaining salts.

Polymerization of **5** required the use of CHP as a solvent medium since higher temperatures could be employed to prevent premature precipitation of the polymers in this case, the water was removed through the Dean-Stark trap with a nitrogen flow through the reaction mixture at 140 °C. Upon dehydration (6–8 h), the polymerization temperatures was increased to 180 °C to effect the displacement reaction. However, the resulting polymers (oligomers) precipitated prior to the formation of high molecular weight. Therefore, it was necessary to raise the temperature to 240–260 °C maintain a homogeneous solution affording high molecular weight in (4–20 h), as judged by the dramatic increase in viscosity. The polymer solutions were diluted with hot with CHP and coagulated in a 10× excess of methanol and washed with boiling water to remove the remaining salts.

These general procedures were applied to a number of bisphenols (**7a–c**) for each of the activated dihalides **3–5**, yielding polymer series **8a–c**, **9a–c**, and **10a–c**, respectively. High molecular weight polymer was achieved in each case as indicated by the intrinsic viscosity measurements (Table I). The three bisphenols chosen were somewhat bulky and should prevent crystallization and impart both solution and melt processability while the high T_g and good thermal stability are retained. NMP solubility is important as NMP is commonly used and is more desirable than other solvents used for rigid high T_g polymers. Polymers **8a–c** and **9a,b** were all soluble in NMP

Scheme IV

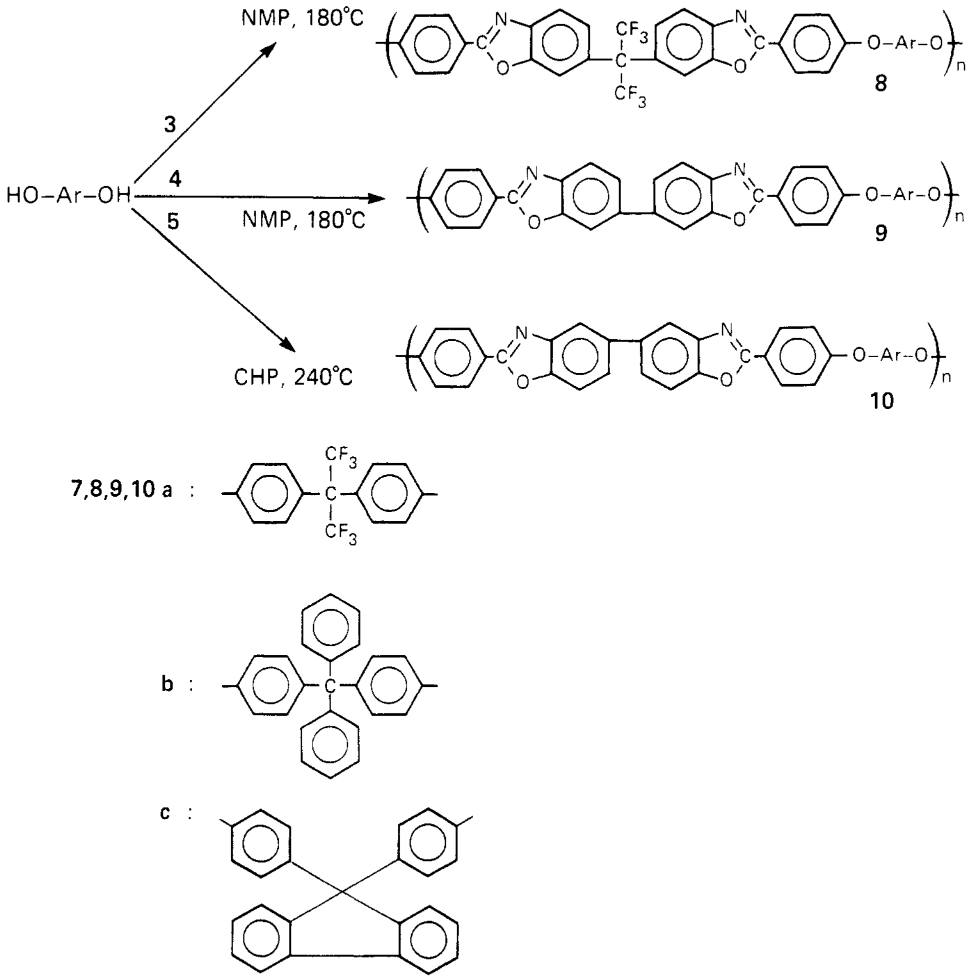


Table I
Characteristics of Poly(aryl ether–benzoazazoles)

polymer	$[\eta]_{25\,°C}{}^{NMP}$	T, °C
8a	0.51	241
8b	0.87	259
8c	0.65	291
9a	0.49	230
9b	0.53	245
9c	1.04[a]	303
10a	*b*	213
10b	0.56[a]	241
10c	*b*	*c*

[a] Viscosity measurement in CHP, 25 °C. [b] Viscosity measurement in CHP not available at room temperature, soluble in CHP above 50 °C. [c] T_g not detectable by DSC.

at relatively high solids composition (15–25 wt %), clearly demonstrating the influence of the aryl ether linkage has on the solubility. Polymers **9c** and **10b** were soluble only in CHP forming highly viscous yellow solutions. Furthermore, these polymers appeared to be aggregated or ordered in solution since the solutions could not be passed through a filter and appeared somewhat turbid. Interestingly, this affect disappeared upon heating where the solutions became clear and less viscous. Polymers **10a** and **10c** did not show the expected solubility in NMP or CHP at room temperature however, they were soluble in CHP at elevated temperatures (>50 °C).

Poly(aryl ether) synthesis is often accompanied by an ether-interchange process. Activated by para electron-withdrawing substituents, aryl ether linkages are subjected to nucleophilic attack, resulting in phenoxide interchange.[8,11,12] The ether interchange process is a major deterrent in preparing block, multiphase poly (aryl ether). Although this process occurs readily for conventional activating groups, we wanted to determine if poly(aryl ether–benzoxazoles) were susceptible to ether interchange. This process was examined by heating **6** with 0.3 equiv of *m*-cresol in CHP in the presence of potassium carbonate at 170 °C. The reaction was monitored by GC, and the product analysis showed the formation of **3** due to exchange of the cresolate for the 4-(*tert*-butylphenoxide) (Figure 2). Approximately 40% of the *m*-cresol had converted to **3** after 24 h demonstrating that poly(aryl ether–benzoxazoles) will undergo ether interchange like conventional poly(aryl ethers).

The structure of the polymers was confirmed by FT-IR and ^{13}C NMR spectroscopy. The FT-IR spectrum of **9a** is shown in Figure 3 with the key characteristics bands pointed out, including the benzoxazole moiety and the ether linkage which is generated in the polymer-forming reaction. The ^{13}C NMR spectrum of **9a** is shown in Figure 4 and consistent with the structure.

The T_g's of the poly(aryl ether–benzoxazoles) ranged from 213 to 303 °C depending on the bisphenol and activated dihalide used in the synthesis (Table I). Generally, the T_g's increased with the bulkiness of the bisphenol used, with **7c** producing the highest T_g polymers. The dynamic mechanical behavior for polymer series **8** is shown in Figure 5. These data, consistent with calorimetry results, clearly show the high T_g's and good dimensional stability exhibited by these materials. In contrast to rigid and semirigid polyimides which do not show a T_g, the poly(aryl ether–benzoxazoles) all manifest a T_g, with no evidence of crystallization, indicative of an amorphous or

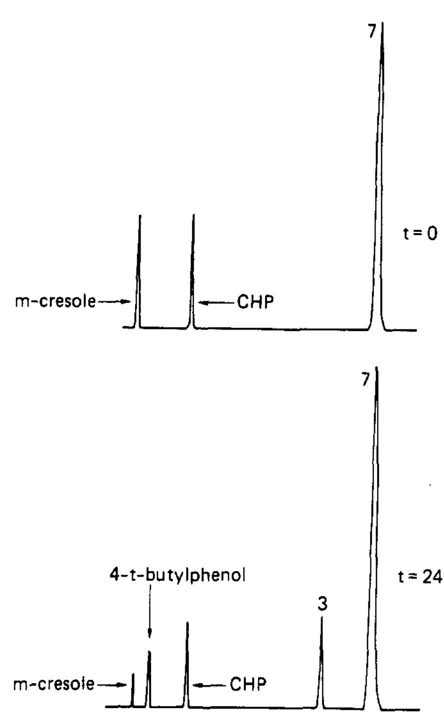


Figure 2. GC analysis of ether interchange of sodium cresolate with (2-(3-*tert*-butylphenoxy)phenyl)benzoxazole in CHP at 170 °C.

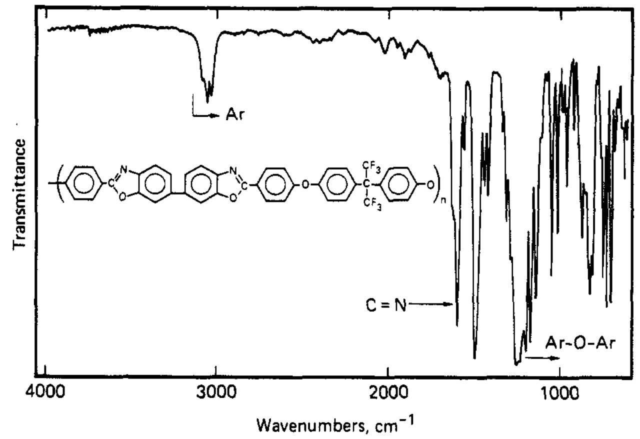


Figure 3. FT-IR spectrum of **9a**.

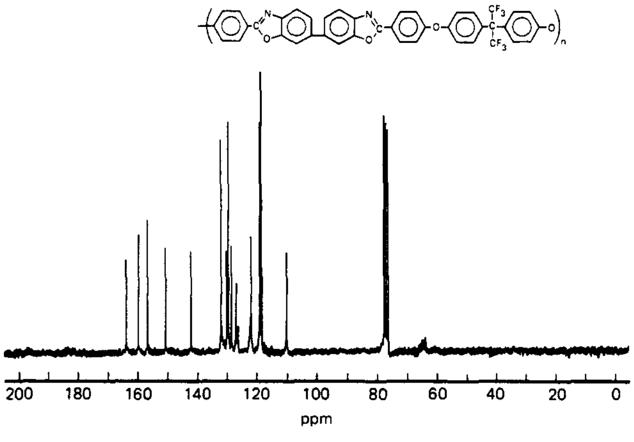


Figure 4. ^{13}C NMR spectrum of **9a**.

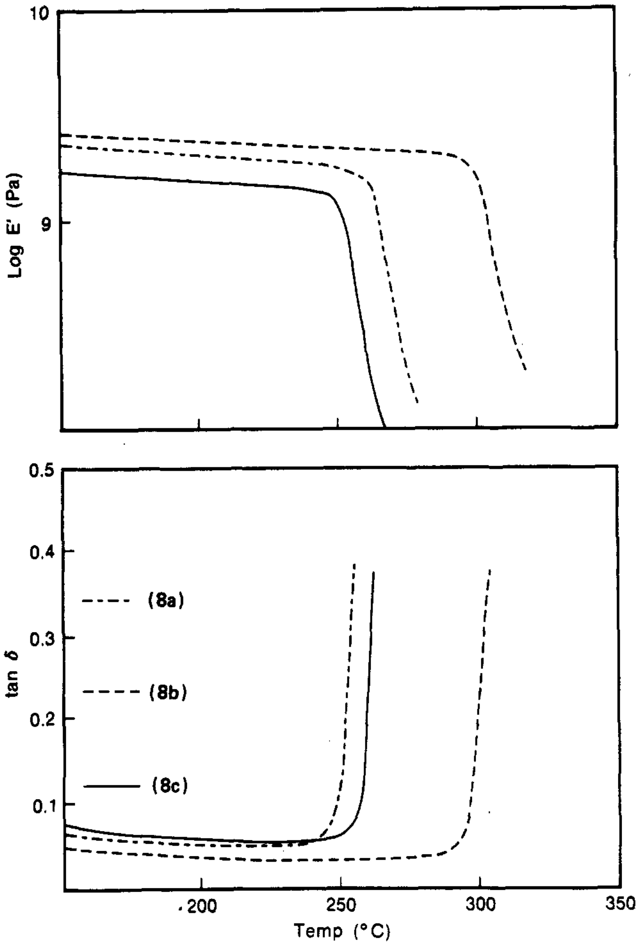


Figure 5. (a) Storage tensile modulus versus temperature. tan δ versus temperature for **8a–c**.

Table II
Thermal Analysis of Poly(aryl ether-benzoxazoles)

polymer	polymer decomp temp[a]	polymer	polymer decomp temp[a]
8a	500	**9c**	520
8b	500	**10a**	500
8c	510	**10b**	510
9a	510	**10c**	530
9b	520		

[a] TGA (5 °C/min), decomposition temperature taken as the inflection point on the TGA curve.

glassy morphology. Furthermore, wide-angle X-ray scattering (WAXS) measurements show no evidence of crystalline or liquid crystalline type morphologies, consistent with an amorphous structure. The T_g's, of these polymers are among the highest reported for poly(aryl ethers) prepared by nucleophilic aromatic substitution, and they are comparable to those reported on the imide and phenylquinoxaline analogues.[7-9]

The poly(aryl ether-benzoxazoles) demonstrated excellent thermal stability with polymer decomposition temperatures in the 500 °C range (Table II). The bisphenol from which the polymer was derived somewhat influenced the thermal stability. Those structures based on **7c** were the most thermally stable as judged by TGA (Figure 6). These data demonstrated that the thermal stability of these structures is comparable to that of the aromatic polyimides and poly(aryl ether-phenylquinoxalines).

The mechanical property measurements for the poly(aryl ether-benzoxazoles) are shown in Table III. In each case, a moduli between 1900 and 2400 MPa were observed which is comparable to many aromatic polyimides (~2000 MPa). The polymers showed yield points with the characteristic stress drop, which is consistent with tough ductile mechanical properties. Although the films were fingernail cresable, they did not all show the expected high elongations. These anomalous results are believed to result from the quality of the thin film specimens rather than

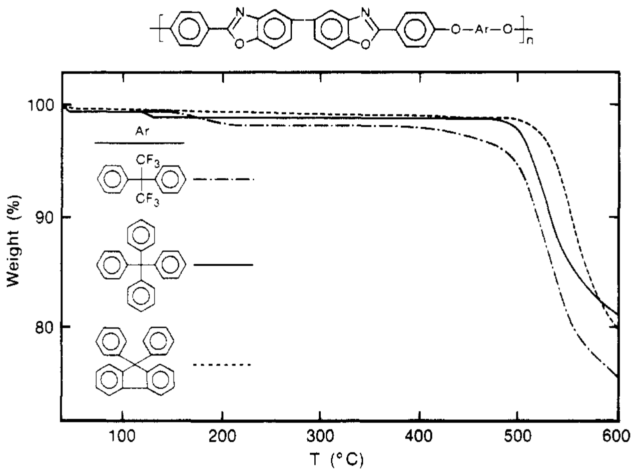


Figure 6. Weight loss versus temperature for poly(aryl ether-benzoxazoles).

Table III
Mechanical Properties of Poly(aryl ether-benzoxazoles)[a]

polymer	modulus, MPa	yield stress, MPa	tensile stress, MPa	elongatn, %
8a	1900	68	74	25
8b	2400	91	83	5
8c	2200	71	70	4
9c	2400	83	85	7
10b	2200	81	74	5

[a] Instron tensile tester, 10 mm/min strain rate.

inherent to the polymer.

The poly(aryl ether–benzoxazoles) behave in many respects as engineering thermoplastics with characteristics similar to those of polysulfone, poly(ether–imide), and others. In contrast to the rigid PBO's, the ether containing benzoxazoles show a large drop in modulus above T_g indicative of an amorphous melt, which allows these materials to be thermoformed 50–70 °C above their T_g. Samples were compression molded at approximately 350 °C, and in spite of their high T_g's, the excellent thermal stability allowed for the high-temperature thermoplastic processing conditions. Since **11a** and **11c** could not be readily processed from solution, melt fabrication allows an alternate method of processing.

Many engineering thermoplastics (e.g. polysulfone, polycarbonate, etc.) have limited utility in applications that require exposure to chemical environments. This is known as environmental stress cracking,[15–17] and this phenomenon occurs when a stressed polymer is exposed to solvents. In an effort to ascertain the environmental stress-cracking resistance of the poly(aryl ether–benzoxazoles), samples were loaded to a constant stress (approximately 40 MPa) in a tensile tester and exposed to different chemical environments (acetone and methylene chloride) for 5 min. Prior to solvent exposure, a small drop in stress was observed due to stress relaxation. Exposure to methylene chloride resulted in catostrophic failure in each of the polymers and exposure to acetone resulted in a reduction of the stress by approximately 50% (Table IV). In each case, significant crazing and cracking were observed, characteristic of a material with poor resistance to environmental stress cracking. This is not entirely unexpected since these structures are amorphous, and there is no crystallinity or liquid crystalline type structure to give solvent resistance. Thus, these materials may have limited utility in processes or applications that require multiple solvent coatings or exposures.

Table IV
Environmental Stress Cracking Resistance of Poly(aryl ether–benzoxazoles)

polymer	solvent	stress, MPa	
		initial	after solvent exposure[a]
8b	acetone	42.0	13.9
8b	methylene chloride	35.8	0
8c	acetone	39.8	14.3
8c	methylene chloride	33.5	0
9c	acetone	43.6	22.3
9c	methylene chloride	45.5	0
10b	acetone	35.2	20.0
10b	methylene chloride	34.1	0

[a] Measured stress after solvent exposure for 5 min.

Conclusions

Poly(aryl ether–benzoxazoles) have been prepared by nucleophilic aromatic substitution in which in the generation of an aryl ether linkages is the polymer forming reaction. We have demonstrated that aryl fluorides para to a 2-benzoxazolyl group were readily displaced with phenoxides. A series of fluoro-substituted bibenzoxazoles were prepared and subjected to fluoro displacement with three different bisphenols in NMP or CHP in the presence of K_2CO_3. High molecular weight was readily achieved yielding polymers that could be processed from solution or the melt. The resulting polymers had T_g's ranging from 213 to 305 °C and thermal decomposition temperatures in excess of 450 °C. This polymerization should provide a general method for preparing aryl ether based benzoxazoles where the structure of the polymer can readily be controlled by varying both the bisphenol and the bis(aminophenol) used. Moreover, heterocyclic activated nucleophilic displacement chemistry should prove effective with monomers derived from other ring systems, providing a general synthetic methodology to high-temperature, high T_g aryl ether–heterocyclic polymers.

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Registry No. **1**, 397-54-6; **2**, 121801-67-0; **3**, 121778-05-0; **4**, 126296-76-2; **5**, 121188-13-4; **6**, 126296-77-3; **8a** (copolymer), 121778-06-1; **8a** (SRU), 121778-50-5; **8b** (copolymer), 126296-

79-5; **8b** (SRU), 126296-87-5; **8c** (copolymer), 126296-80-8; **8c** (SRU), 126296-88-6; **9a** (copolymer), 121778-04-9; **9a** (SRU), 121778-49-2; **9b** (copolymer), 126296-81-9; **9b** (SRU), 126296-89-7; **9c** (copolymer), 126296-82-0; **9c** (SRU), 126296-90-0; **10a** (copolymer), 126296-83-1; **10a** (SRU), 126327-52-4; **10b** (copolymer), 126296-84-2; **10b** (SRU), 126296-91-1; **10c** (copolymer), 126296-85-3; **10c** (SRU), 126296-92-2; 4-fluorobenzoyl chloride, 403-43-0; 2-aminophenol, 95-55-6; *m*-cresol, 108-39-4; 2,2′-bis(3-amino-4-hydroxyphenyl)hexafluoropropane, 83558-87-6; 4-fluorobenzoic acid, 456-22-4; 4,4′-amino-3,3′-hydroxybiphenyl, 2373-98-0; 3,3′-diamino-4,4′-dihydroxybiphenyl, 4194-40-5; 4-*tert*-butylphenol, 98-54-4.

Synthesis of Telechelic Poly(tetrahydrofuran) Having a Carboxyl Group by Using an Anion of Diethyl Malonate or Hydroxy Esters as Terminator

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ABSTRACT: Telechelic poly(tetrahydrofurans) (polyTHFs) having ester groups at each polymer end have been prepared by terminating living propagating species with an anion of diethyl malonate or of a hydroxy-containing ester. The resulting polymers have been converted into the corresponding telechelic polyTHFs having aliphatic or aromatic carboxyl groups by the hydrolysis and successive decarboxylation of the terminal diethyl malonate moiety or by the hydrolysis of the terminal ester moiety. The functionality of the resulting polyTHFs is close to 2.0, indicating that two carboxyl groups have quantitatively been introduced onto both polymer ends.

Introduction

Telechelic poly(tetrahydrofuran) (polyTHF) is an important building block for construction of various polymer materials such as a polyurethane and polyester. It is well-known that THF is polymerized by trifluoromethanesulfonic anhydride ($(CF_3SO_2)_2O$) as a bifunctional initiator to give a living polymerization system having tetrahydrofuranium species at the polymer ends.[1]

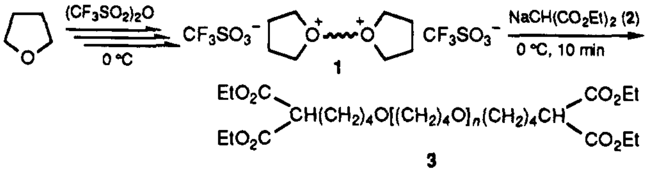
Telechelic polyTHFs having a variety of functional groups are usually prepared by reaction of the living propagating species with various nucleophiles.[2] Poly(oxytetramethylene) glycol, the most widely used telechelic polyTHF having terminal hydroxyl groups, can be synthesized by termination of the living species with water. Telechelic polyTHF of a bis-primary amine type can be produced by reaction of the living species with excess ammonia as terminator.[1]

Recently, much attention has been paid to telechelic polyTHFs having carboxyl groups. The telechelic polymer may be utilized as a starting material for various high-performance polymers with oxytetramethylene units in the main chain. In the previous paper, we have reported a new method for the preparation of telechelic polyTHFs having carboxyl groups, which involves a nucleophilic termination reaction of a ketene silyl acetal or a ketene bis(silyl acetal) with the living propagating species.[3] In relation to the present study, it has been reported that the oxidation of poly(tetrahydrofuran) glycol by a Cr(VI) compound gave telechelic polyTHF with a carboxylic acid group.[4]

The present paper describes a convenient synthesis of telechelic polyTHFs having carboxyl group using an anion of diethyl malonate or of a hydroxy-containing ester (hydroxy ester).[5] The introduction of carboxyl groups onto the polymer ends has been achieved by the following two reactions. The first is the termination of the living propagating species of THF with an anion (sodium salt) of diethyl malonate[6] or of a variety of hydroxy esters, giving rise to the corresponding end-capped telechelic polyTHFs having ester groups. The second is the conversion of the ester groups into carboxyl groups by hydrolysis and/or decarboxylation.

Results and Discussion

Synthesis of Telechelic PolyTHF Having Terminal Ester Groups by Using Sodium Diethyl Malonate as Terminator. THF was polymerized at 0 °C using $(CF_3SO_2)_2O$ as a bifunctional initiator to afford the living THF polymer **1**. The sodium salt of diethyl malonate, **2**, was very reactive toward the living ends of **1**, and the reaction was completed within 10 min at 0 °C. After work-up procedures, telechelic polyTHF **3** having a diethyl malonate moiety at both polymer ends was obtained.



The structure of **3** was confirmed by ^1H and ^{13}C NMR spectroscopies (Figure 1). The hydroxyl group would be contained as the terminal group in **3** if the living propagating species of THF was not quantitatively reacted with **2**. No signals due to the α-methylene carbon and β-me-