Poly(aryl ether benzothiazoles)

Polybenzothiazoles (PBT) are among the most thermally stable polymers reported, and the high degree of molecular rigidity in the backbone produces high-modulus polymers with applications as fibers and multilayer circuit boards.[1] PBT's are generally synthesized by the polycondensation of a carboxylic acid derivative with an *o*-aminothiophenol derivative, where the benzothiazole ring formation is the polymer-forming reaction.[1,2] The polymerizations are generally conducted in poly(phosphoric acid) (PPA) which solvates the monomer(s), subsequent oligomers, and the polymer formed, activates both functional groups toward condensation, and reacts with the water formed by the condensation to effectively dehydrate the system. Although high polymer may be obtained in strong acidic media, processing by conventional methods is difficult. Due to the limited solubility and melt processability, processing is primarily limited to wet extrusion and several variations of this process.

It has been generally recognized that aromatic ether linkages in the polymer backbone provide improved solubility and processability as well as lower the T_g and subsequent processing temperatures.[3] Most poly(aryl ethers) display excellent solubility characteristics while retaining the desired thermal stability and mechanical properties. Examples of high-temperature polymers which have been favorably modified by the incorporation of aryl ether linkages include imides,[4] phenylquinoxalines,[5,6] benzoxazoles,[7,8] and oxadiazoles.[9,10] Likewise, it seemd plausible that PBT could also be modified by the incorporation of aryl ether constituents. As a route to this polymer, a poly(aryl ether) synthesis should be possible where the benzothiazole heterocycle activates an aromatic halo displacement reaction with phenoxides, generating an aryl ether linkage as the polymer-forming reaction. In this paper, the thiazole-activated halo displacement is investigated as well as the use of this reaction to prepare novel poly(aryl ether benzothiazoles).

The synthesis of poly(aryl ethers) is based on the nucleophilic aromatic displacement of an aryl halide (nitro) with a phenoxide in polar aprotic solvents.[11] The aryl halide (nitro) substituent is activated by an electron-withdrawing group such as carbonyl or sulfone. In addition, we have recently demonstrated that selected heterocycles (i.e., phenylquinoxaline,[5] benzoxazoles,[8] and oxadiazole[10]) are also effective activating groups for polyether syntheses. The characteristics common to these activating groups are that they are electron withdrawing and have a site of unsaturation, which can stabilize the negative charge developed in the displacement through resonance to a heteroatom. This involves the formation of a Meisenheimer complex, which lowers the activation energy for the displacement reaction.[10,11] The rationale for the thiazole-activated halo displacement is similar to that of the oxazole-activated displacement and is derived from both the electron affinity and stabilization of the negative charge developed in the transition state through the formation of a Meisenheimer complex, analogous to conventional activating groups as shown in Scheme I. The effectiveness of a thiazole heterocycle as an activating group can be estimated using ^{1}H NMR, where the chemical shift of the aromatic protons ortho to the thiazole ring may be used to estimate the electron affinity, as previously published for other new activating groups.[5,8,12] ^{1}H NMR shows the ortho protons of the 2-phenyl ring (δ 8.2) of compound **1**[13] to be further downfield than the ortho protons of the benzo ring (δ 7.5 and 7.9), indicating that the thiazole heterocycle has a greater effect on the 2-phenyl group than the benzo ring of the benzothiazole (Figure 1). The electronic effect of the thiazole ring is analogous to the oxazole group which activated a fluoro-displacement polymerization used to prepare poly(aryl ether benzoxazoles). Furthermore, ^{1}H NMR shows the deshielding of the aromatic protons ortho to the benzothiazole ring (δ 8.2) versus a ketone group (δ 7.9) to be greater with respect to electron affinity, which further indicates the possibility of facile displacement at the 4-position of the 2-phenyl ring of compound **1**.[5,8]

To demonstrate the feasibiliy of the benzothiazole-activated aryl ether synthetic approach for the preparation of poly(aryl ether benzothiazoles), a model reaction between **1** and *m*-cresol was investigated in a *N*-methyl-2-pyrrolidone/*N*-cyclohexyl-2-pyrrolidone (NMP/CHP) solvent mixture in the presence of potassium carbonate (Scheme II). CHP was used as a cosolvent since it is not miscible with water at temperatures above ~100 °C, and, interestingly, this affect is observed even if CHP is used as a cosolvent at low compositions, precluding the need for a lower boiling cosolvent to azeotrope the water generated upon phenoxide formation.[5,8] Potassium carbonate was used to form the phenoxide, and since potassium carbonate is a weak base, possible hydrolytic side reactions of the aryl fluoride are avoided. The reaction mixture was heated to 150 °C (6 h), where the water generated by phenoxide formation was effectively removed and collected in a Dean–Stark trap. Upon dehydration, the reaction temperature was increased to 185 °C to effect the displacement reaction (20 h). Quantitative conversion of **1** was observed with the formation of a single product by TLC (ethyl acetate/hexane). The resulting product was isolated in 90% yield with spectral characteristics and C, H, and N values consistent with the assigned structure, 2-[4-(3-methylphenoxy)phenyl]benzothiazole (**2**).[14] The model reaction demonstrated that the fluoro group is readily displaced by phenoxides as a result of activation by the thiazole heterocycle. This transformation occurred with high selectivity and was clearly suitable as a polymer-forming reaction.

The preparation of the poly(aryl ethers) containing the preformed benzothiazole rings required the synthesis of a bis(fluorophenyl)dibenzothiazole to react with various bisphenols. For our experiments we prepared 2,6-bis(4-fluorophenyl)benzo[1,2-*d*:4,5-*d'*]bisthiazole (**3**) synthesized by the reaction of 1,4-dimercapto-2,5-diaminobenzene dihydrochloride with an excess of 4-fluorobenzoyl chloride in the presence of excess triethylamine (used as an acid acceptor as well as to deprotect the amino groups) in chloroform (–5 °C) (Scheme III). The reaction was slowly heated to reflux temperatures for 3 h where the solution became clear. The chloroform solution was cooled, partitioned with water, washed, and isolated. Quantitative conversion of 1,4-dimercapto-2,5-diaminobenzene was observed (HPLC) with the formation of a single product peak. The resulting yellow powder was placed in a vessel for sublimation and slowly heated to 260 °C to effect ring closure. The powder was observed to melt at approximately 200–225 °C, and upon ring closure 4-fluorobenzoic acid was evolved; the crude product solidified into a dark crystalline powder (Scheme III). Recrystallization from NMP (twice) afforded **3** as a polymer-grade monomer.[15] It is important to note that the use of 2,5-diamino-1,4-benzenethiol dihydrochloride affords a bis(fluorophenyl)-bisbenzothiazole in the trans conformation. It has been shown that benzothiazole homopolymers prepared with the trans conformation are composed of rigid segments

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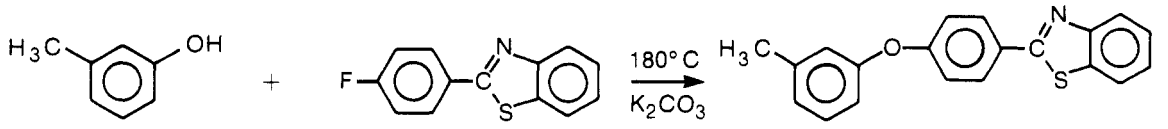
Scheme I



1 2

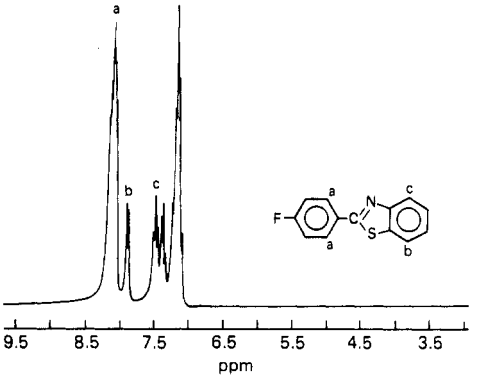
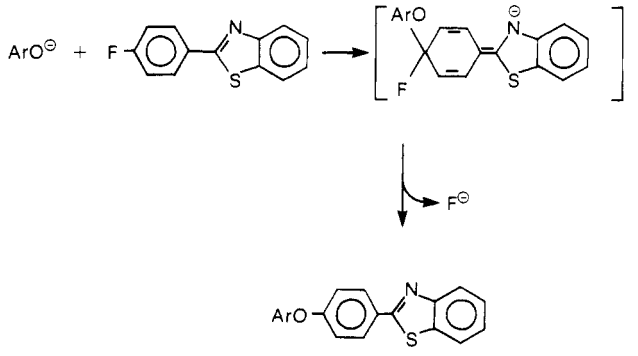


Figure 1. ^{1}H NMR of compound 1.

Scheme II

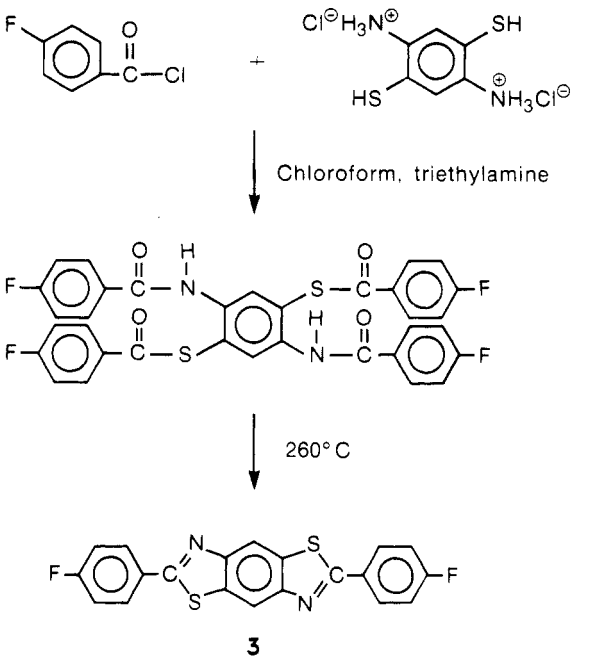


with catenation angles of nearly 180°.[1]

Polymerization of **3** with Bisphenol AF (**4a**) was carried out in the presence of K_2CO_3 in an NMP/CHP solvent mixture according to literature procedures (Scheme IV). During the initial stage of the polymerization, the reaction temperature was maintained at approximately 150 °C and the water generated by bisphenoxide formation was removed from the system and collected in a Dean–Stark trap. This procedure usually took 5–7 h and, upon completion, the polymerization temperature was increased to 190–195 °C to effect the displacement reaction. High polymer was obtained within 4–6 h as judged by a dramatic increase in viscosity. In fact, the polymerization dope was observed to climb the stirring rod as the polymerization approached completion. However, it is important to note that the resulting polymer appeared to remain soluble during the latter stages of the polymerization. The resulting polymer (**5a**) was coagulated in excess methanol and dried. Alternatively, diphenyl sulfone, a higher boiling solvent, was also investigated as a polymerization medium. However, precipitation occurred early in the polymerization, precluding the formation of high molecular weight polymer.

This general polymerization procedure of **3** was applied to a number of bisphenols (**4a–d**), affording poly(aryl ether benzothiazoles) **5a–d**. The resulting polymers showed high T_g's consistent with the values of other heterocyclic-containing poly(aryl ethers). The viscosity values for polymers **5a** and **5c** were 0.46 and 0.80 dL/g, respectively, and considered high for a poly(aryl ether). For comparison,

Scheme III

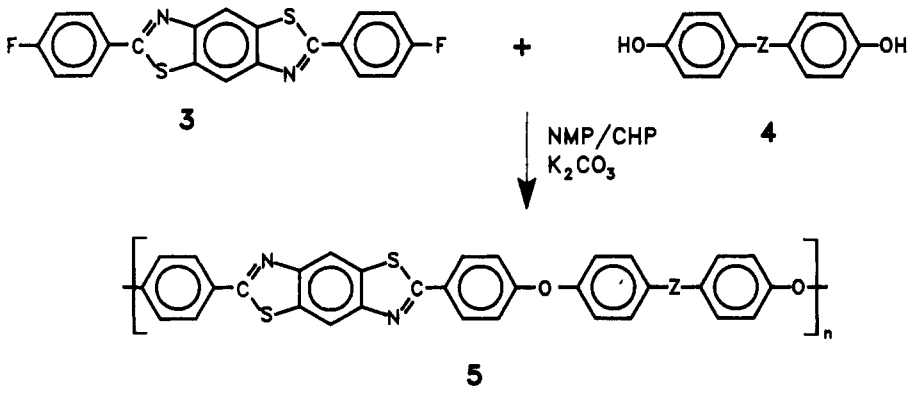


3

the commercially available poly(aryl ether sulfone) has an intrinsic viscosity of 0.48 dL/g in NMP. However, unlike other poly(aryl ethers) where the incorporation of the aryl ether linkage imparts solubility, the poly(aryl ether benzothiazoles) showed little solubility in organic solvents at room temperature and only marginal solubility at high temperatures. Therefore, intrinsic viscosity values for polymers **5b** and **5d** were unobtainable due to their limited solubility in NMP and other solvents. Films of the poly(aryl ether benzothiazoles) were fabricated by compression molding approximately 50 °C above their T_g's. The resulting films were, in some cases, somewhat brittle which may be attributed to the rigid nature of the benzothiazole-containing repeat unit or to the limited solubility of the polymers, precluding the formation of very high molecular weight polymer even at the high polymerization temperatures. In these cases, the high intrinsic viscosity values may be a manifestation of the rigid nature of the poly(aryl ether benzothiazoles).

As a means of preparing a more soluble/processable poly(aryl aryl benzothiazoles), random copolymers were prepared where the benzothiazole-containing difluoride **3** was systemically replaced with various compositions of 4,4′-difluorodiphenyl sulfone (**6**) and polymerized with **4a** (Scheme V). The polymerizations were conducted in an analogous fashion to the synthetic procedure described above, and the characteristics of the subsequent copolymers (**7–9**) are shown in Table I. The composition of aryl ether benzothiazole or **3** was maintained at weight percents of 10, 25, and 50 relative to the weight of **6**, producing copolymers **7–9**, respectively. The T_g's of the copolymers ranged from 210 to 230 °C depending on the sulfone weight percent or composition, and the molecular

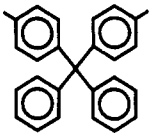
Scheme IV



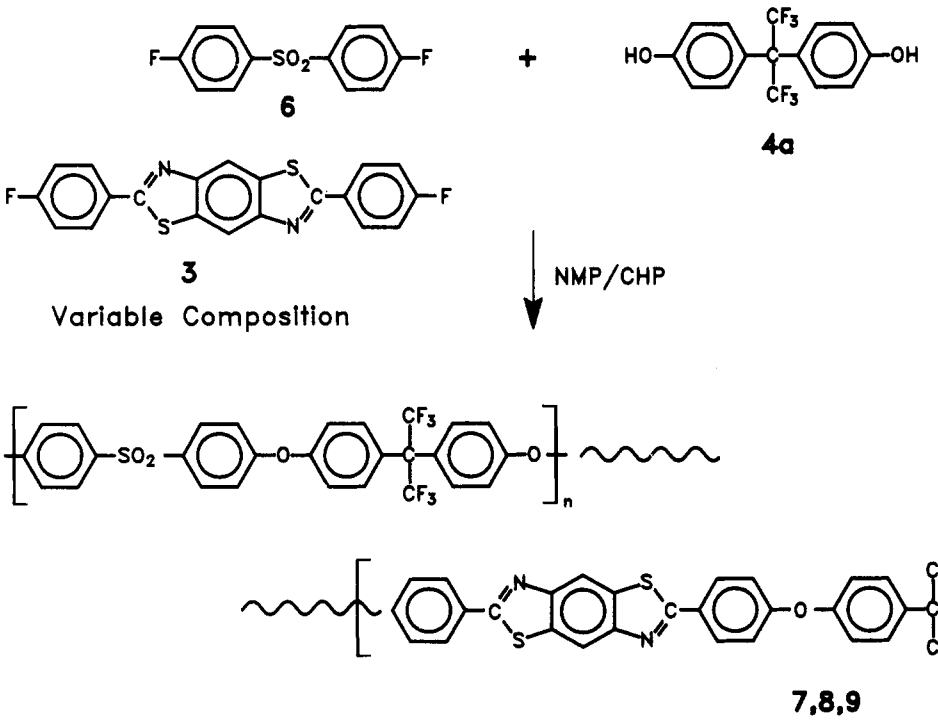
3 4 5

Z

4,5 : a = $C(CF_3)_2$
: b = $C(CH_3)_2$
: c = $C(CPh)_2$
: d =



Scheme V



6 4a 3 7,8,9

Copolymer

Composition of 3 (wt. %):		
	10 =	7
	25 =	8
	50 =	9

weights were high as judged by the intrinsic viscosity measurements (Table I). Films of the copolymers showed improved toughness, particularly at the lower benzothiazole compositions.

Poly(aryl ether benzothiazoles) have been prepared by a nucleophilic aromatic substitution polymerization, generating an aryl ether linkage as the polymer-forming reaction. We have demonstrated that the electron-deficient thiazole heterocycle activated fluoro substituents toward displacement with a variety of nucleophiles. The appropriately substituted thiazole monomer was prepared and subjected to the displacement polymeriza-

Table I
Characteristics of Poly(aryl ether benzothiazoles) and Copolymers

entry no.	$[\eta]_{NMP}^{25°C}$, dL/g	T_g, °C	entry no.	$[\eta]_{NMP}^{25°C}$, dL/g	T_g, °C
5a	0.83	240	7	1.01	204
5b	*a*	248	8	0.68	214
5c	0.48	250	9	0.89	222
5d	*a*	*b*			

[a] Not soluble in NMP. [b] Not detectable by DSC.

tion with various bisphenols in the presence of potassium carbonate in an NMP/CHP solvent mixture. The resulting polymers showed high T_g's and polymer decomposition temperatures in the 450 °C range. Improved processibility was demonstrated by a random copolymerization with difluorodiphenyl sulfone. This thiazole-activated fluoro displacement represents another example of the synthesis of poly(aryl ethers) based on a heterocycle-activated halo displacement, and this synthesis can be considered the thiazole analogue of the poly(ether imide) synthesis. Moreover, the heterocycle-activated nucleophilic displacement chemistry provides a general methodology to other high-temperature, high-T_g poly(aryl ethers).

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(13) 2-(4-Fluorophenyl)benzothiazole, (1) mp = 96–98 °C; IR (KBr) 1604, 1502, 1455, 1436, 1296, 1252 cm^{-1}. Anal. Calcd for $C_{13}H_8N_1S_1F_1$: C, 68.10; H, 3.52; N, 6.11. Found: C, 68.01; H, 3.53; N, 5.69.
(14) 2-[4-(3-Methylphenoxy)phenyl]benzothiazole (**2**). Anal. Calcd for $C_{20}H_{15}O_1S_1N_1$: C, 75.69; H, 4.76; N, 4.41. Found: C, 75.41; H, 4.02; N, 4.82.
(15) 2,6-Bis(4-fluorophenyl)benzo[1,2-*d*:4,5-*d'*]bisthiazole (**3**) mp = 314–317 °C; IR (KBr) 1526, 1426, 1411, 1311, 1209 cm^{-1}. Anal. Calcd for $C_{20}H_{10}N_2S_2F_2$: C, 63.14; N, 7.36; H, 2.65. Found: C, 63.01; N, 7.36; H, 2.73.

James L. Hedrick

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

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