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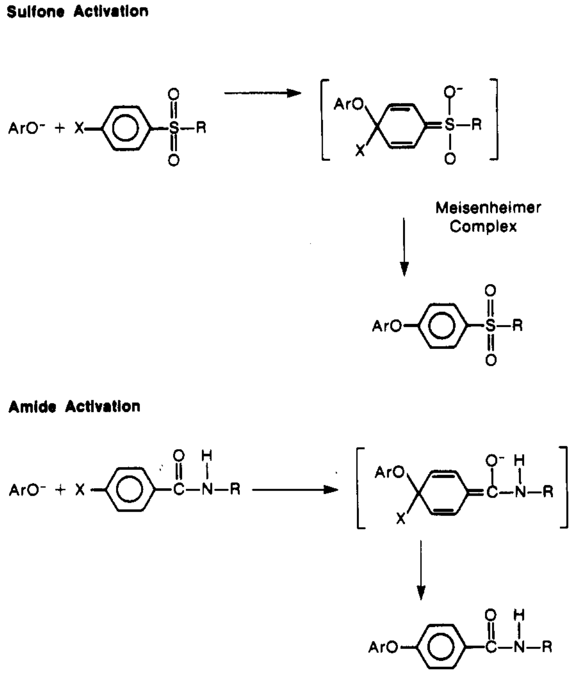
# Poly(aryl ether amides)

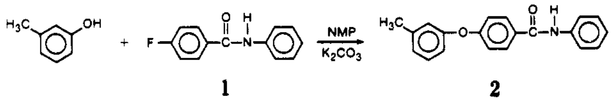
Poly(aryl ethers) and related structures comprise a class of engineering thermoplastics exhibiting many desirable characteristics, which include tough ductile mechanical behavior, high glass transition temperatures, processability from either the melt or solution, and good thermal stability. Poly(aryl ethers) are generally synthesized by the step growth polymerization of activated aryl dihalo or dinitro monomer with bisphenoxides, where the generation of an aryl ether linkage is the polymer-forming reaction.[1-3] It has been demonstrated that both sulfone and ketone groups are effective in activating aryl halides toward nucleophilic displacement and used in the preparation of poly(aryl ether sulfones)[1] and semicrystalline poly(aryl ether ketones),[2] respectively. Heterocyclic rings (i.e., imides,[3] quinoxalines,[4] and benzoxazoles[5]) and fluoroalkyl groups[6] have also been used as activating groups to produce new poly(aryl ethers). A common characteristic of these activating groups is their electron-withdrawing character and the presence of a site of unsaturation, which can stabilize the negative charge developed in the displacement through resonance to an electronegative atom. This requires the formation of a Meisenheimer complex, which lowers the activation energy of the displacement reaction.[1,2]

It is of interest to investigate other activating groups such as an amide, which will produce new poly(aryl ethers). The electron-withdrawing amide moiety should activate 2- or 4-aryl halo substituents toward nucleophilic aromatic substitution. Facile displacement should occur at these positions since the amide group can stabilize the negative charge developed in the transition state through a Meisenheimer complex, analogous to conventional activating groups (e.g., sulfone, carbonyl) as shown in Scheme I. The effectiveness of an amide as an electron-withdrawing group can be estimated by both the Hammett $\sigma$ value and the chemical shift of aromatic protons ortho to the amide substituent, as previously published for other new activating groups.[4-7] Comparison of Hammett $\sigma$ values of the amide group to a ketone group, 0.36 and 0.50, respectively, shows them to be electronically similar. Furthermore, $^{1}$H NMR shows the deshielding of the aromatic protons ortho to the amide group ($\delta$ = 8.1) versus a ketone group ($\delta$ = 7.9) to be greater with respect to the electron affinity and further portends the likelihood of facile displacement at the 4-position. Poly(aryl ether amides) and similar copolymers have previously been reported;[8] however, these syntheses involved the reaction of bisphenols containing performed amide linkages with conventional activated halides in *N*-methyl-2-pyrrolidone (NMP) in the presence of $K_2CO_3$. This synthetic approach demonstrated that the amide linkage survived typical polycondensation reaction conditions, and the subsequent polymers and copolymers showed enhanced solvent resistance compared to other amorphous poly(aryl ethers). In this paper the investigations of amide-activated fluoro displacement and the application of this as a polymer-forming reaction to prepare poly(aryl ether amides) will be discussed.

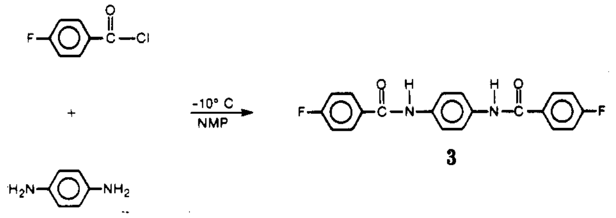
Scheme I



Scheme II



Scheme III



To demonstrate the feasibility of the amide-activated halo displacement, a model reaction between *N*-(4-fluorobenzoyl)aniline (**1**)[9] and *m*-cresol was carried out in a NMP/toluene solvent mixture in the presence of $K_2CO_3$ (Scheme II).[5,10] During the initial stages of the reaction, the water generated by the phenoxide formation was removed as an azeotrope with toluene (150 °C). Upon completion of phenoxide formation and dehydration (4-6 h), the reaction mixture was heated at 180 °C to effect the displacement reaction. Quantitative conversion of **1** was observed with the formation of a single product peak. The product was isolated in high yield (>90%) and recrystallized (ethyl acetate/hexane) to afford a light yellow crystalline solid with the spectral properties and C, H, and N analysis characteristic of the expected *N*-[4-(3-methylphenoxy)benzoyl]aniline (**2**; mp = 137-139 °C).[11] The model reaction demonstrated that the 4-fluoro group is readily displaced by phenoxides, as a result of the activation by the amide group. The transformation occurred with high selectivity and was judged suitable as a polymer-forming reaction.

In order to demonstrate the plausibility of the amide-activated fluoro displacement to prepare high molecular weight poly(aryl ether amides), the appropriate bis(4-fluoroamide)-based monomer was prepared. The synthesis involved the reaction of 4-fluorobenzoyl chloride with 1,4-phenylenediamine (PDA) in THF with triethylamine as an acid acceptor (Scheme III). The 4-fluorobenzoyl chloride was added dropwise to the solution of PDA and triethylamine (-5 °C) and, upon addition, a precipitate formed. The precipitate was isolated by filtration and rinsed with water and methanol to remove both the salts and excess 4-fluorobenzoic acid, respectively. The resulting 1,4-bis(4-fluorobenzamido)benzene (**3**) was isolated in 90% yield and was recrystallized twice (NMP) to afford a white crystalline powder (mp = 344-347 °C). The spectral properties and C, H, and N analysis were

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**Scheme IV**

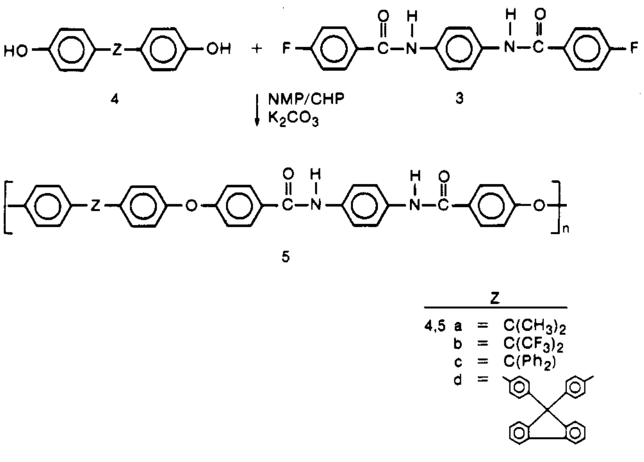
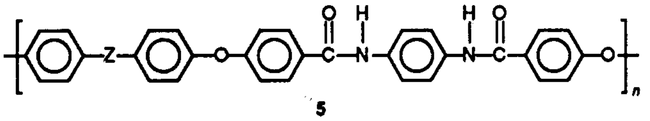
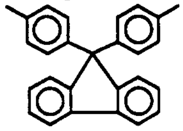


**Table I**
**Characteristics of Poly(aryl ether amides)**



**5**

| sample | Z | NMP [η] at 25 °C, dL/g | $T_g$, °C |
|---|---|---|---|
| **5a** | $C(CH_3)_2$ | 0.60 | 230 |
| **5b** | $C(CF_3)_2$ | 0.42 | 218 |
| **5c** | $C(Ph)_2$ | 0.73 | 254 |
| **5d** |  | 0.43 | |

consistent with the assigned structure.[12] It should be pointed out that prior to further transformations **3** was dried in a vacuum oven at room temperature in the presence of $P_2O_5$ (24 h) and then alone at 150 °C (24 h) to ensure complete water removal.

Polymerization of **3** with Bisphenol AF (**4a**) was carried out in the presence of $K_2CO_3$ (excess) in an NMP/*N*-cyclohexyl-2-pyrrolidone (CHP) (1/1) solvent mixture according to literature procedures (Scheme IV).[4,5] Unlike most polyether syntheses where toluene is used as the azeotroping agent, in this case toluene was not entirely suitable as the dehydrating agent since it interfered with the solvation of **3**. Instead, CHP was used as a cosolvent since at temperatures above 80 °C it becomes immiscible with water and effectively dehydrates the system.[5] 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 through a Dean–Stark trap. Upon completion of bisphenoxide formation and dehydration (4–7 h), the polymerization temperature was increased to 180–190 °C to effect the displacement reaction. High polymer was obtained within 10 h as judged by the dramatic increase in viscosity. The resulting polymer (**5a**) was coagulated in an excess water/methanol (50/50) solvent mixture, subjected to the appropriate solvent rinses, and dried in a vacuum oven (80 °C) for 24 h.

This general procedure was applied to several bisphenols (**4a–d**) affording high molecular weight materials (**5a–d**), as indicated by the intrinsic viscosity measurements (Table I). The intrinsic viscosity values ranged from 0.42 to 0.73 dL/g, typical values for a high molecular weight poly(aryl ether). For comparison, the commercially available poly(aryl ether sulfone) (UDEL) has an intrinsic viscosity of 0.48 dL/g in NMP. It is important to note that if **3** was not properly dried, viscosities above 0.4 dL/g were not obtained. Unlike other poly(aryl ethers), the poly(aryl ether amides) were not soluble in chloroform, THF, or other common organic solvents but only in aprotic dipolar solvents (i.e., NMP, CHP, etc.). This improved solvent resistance is consistent with the previous report.[8]

The glass transition temperatures ranged from 218 to 254 °C depending on the bisphenol used in the synthesis (Table I). Interestingly, these values are considerably higher than those of the poly(aryl ether sulfone) and poly(aryl ether imide) analogues, consistent with the expected affect of hydrogen bonding. However, the calorimetry measurements showed no evidence of crystallinity. The thermal stability, as assessed by the polymer decomposition temperature (5 °C/min of heating rate), of polymers **5a** and **5c** showed decomposition temperatures of 420 and 410 °C, respectively. Thus these polymers should be amenable toward melt processing in spite of their high $T_g$.

The results demonstrated that amide-based poly(aryl ethers) can be synthesized by a fluoro displacement polymerization, where the amide linkage is the activating group. The polymerization provides a general method for the preparation of aryl ether based polyamides, where the structure is readily controlled by varying the bisphenol used. Future work on the poly(aryl ether amides) will focus on demonstrating the scope of materials possible by utilizing other bisamide monomers as well as other bisphenols. In addition, the use of this amide-activated fluoro displacement to produce high-temperature polymer intermediates (i.e., benzoxazoles, oxadiazoles, hydrazines, etc.) will also be investigated.

## References and Notes

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(9) The synthesis of 1 was carried out by the reaction of aniline with 4-fluorobenzoyl chloride in chloroform in the presence of triethylamine; mp = 186–188 °C. Anal. Calcd for $C_{13}H_{10}N_1F_1O_1$: C, 72.57; H, 4.75; N. 6.87. Found: C, 72.59; H, 4.70; N, 6.63.

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(11) Anal. Calcd for $C_{20}H_{17}O_2N_1$: C, 79.18; H, 5.65; N, 4.61. Found: C, 79.47; H, 5.65; N, 4.70.

(12) Anal. Calcd for $C_{20}H_{14}N_2O_2F_2$: C, 68.17; H, 4.00; N, 7.95. Found: C, 67.88; H, 4.01; N, 8.12.

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