

## **Poly(aryl ether amides): Self polymerization of an A-B monomer via amide-activated ether synthesis**

**M. Lucas and J. L. Hedrick\***

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

### **Summary**

A synthetic approach for the preparation of poly(aryl ether amides) has been developed where the generation of an aryl ether linkage was the polymer-forming reaction. The amide moiety was found to be sufficiently electron withdrawing to activate halo-substituents, towards nucleophilic aromatic substitution polymerizations, analogous to conventional activating groups (i.e. sulfone, ketone etc.). Several new A-B monomers, 4-fluoro-N-(4-hydroxyphenyl)benzamide, **1**, and 4-fluoro-N-(3-hydroxyphenyl)benzamide, **2**, which contain both an amide-activated fluoro group and a phenol group were prepared and their self polymerization studied. Compounds **1** and **2** were prepared by the condensation of 4-fluorobenzoyl chloride with either 4- or 3-aminophenol, respectively. The polymerizations were carried out in an N-methyl-2-pyrrolidone (NMP)/N-cyclohexyl-2-pyrrolidone (CHP) solvent mixture in the presence of potassium carbonate. Several new high molecular weight poly(aryl ethers) were prepared by this route with T<sub>g</sub>'s in the 225 °C range.

### **Introduction**

Aromatic polyamides are generally prepared by the reaction of aromatic diamines with aromatic diacid chlorides by either a solution or an interfacial polymerization technique (1). The preferred route to aromatic polyamides is the solution polycondensation in amide solvents, since advantages in molecular weight, molecular weight distribution and polymer solubility are realized. As polymerized, the aromatic polyamides remain soluble in amide solvents and the solubility is enhanced by the addition of lithium chloride; however, upon isolation the polymers are no longer soluble in organic solvents rather strong acids must be used. Therefore, in the case of an interfacial polymerization where the product usually precipitates from the organic medium subsequent solution processing is difficult. Furthermore, since many of the aramid related materials have melting or softening transitions close to their decomposition temperatures, melt processing is also limited.

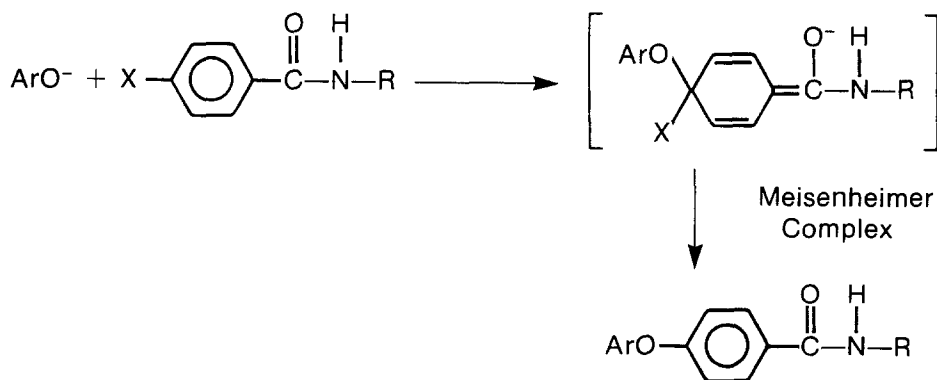
The introduction of ether linkages is known to improve the solubility characteristics of rigid polymers. An efficient means of introducing ether linkages in rigid heterocycle-containing polymers is through a poly(ether) synthesis, where the desired preformed heterocycle is introduced in the bisalide or bisphenol monomer. An important example of this approach is the synthesis of poly(ether-imide) via nitro-displacement polymerization of bis(nitrophthalimides) with bisphenols (2). Poly(ether-imides) are engineering thermoplastics that have excellent solution and melt processability relative to rigid polyimides. Likewise, Hedrick et al.(3) have demonstrated the synthesis of poly(aryl ether phenylquinoxalines) by the polymerization of bis(fluorophenylquinoxalines) with bisphenols. This polymerization was based on the activation of the fluoro-group towards nucleophilic aromatic substitution by the pyrazine component of the quinoxaline

\*To whom offprint requests should be sent

heterocycle. The resulting polymers could be processed from common organic solvents or the melt.

This synthetic approach has been extended to the preparation of poly(aryl ether amides) which are soluble in typical aprotic dipolar solvents and have Tg's in the 225 °C range. (4). The amide moiety was found to be sufficiently electron withdrawing to activate aryl fluorides towards nucleophilic aromatic substitution polymerization with bisphenoxides generating an aryl ether linkages as the polymer forming reaction. Since the amide is a carboxylic acid derivative it is expected to be a good activating group. Comparison of the Hammett  $\sigma$  values of an amide to a ketone (a known effective activating group), 0.36 and 0.50, respectively, and the chemical shift of the protons, ortho to an aromatic amide and ketone, 8.1 and 7.9, respectively, shows them to be electronically similar (4). Furthermore, the polymerization demonstrated that the amide moiety is an effective activating group for the displacement due to the stabilization of the negative charge developed in the transition through the formation of a Meisenheimer Complex, analogous to other activating groups (5,6) (i.e., ketone, sulfone etc.) (Scheme 1). Since the polymer-forming reaction involves the polycondensation of an aryl fluoride with a phenoxide, the amide-activated ether synthesis should be amenable towards the preparation and self-polymerization of an A-B monomer. In this communication several new A-B monomers, 4-fluoro-N-(4-hydroxyphenyl) benzamide, 1, and 4-fluoro-N-(3-hydroxyphenyl) benzamide, 2, have been prepared and their self-polymerization investigated.

### Amide Activation



Scheme 1

### Experimental

#### Materials

Anhydrous N-Methyl-2-pyrrolidone, NMP, and N-Cyclohexyl pyrrolidone, CHP, were used as received (Aldrich). 4-Aminophenol, 3-aminophenol and 4-fluorobenzoyl chloride were used without further purification (Aldrich).

#### Monomer Synthesis

4-fluoro-N-(4-hydroxyphenyl)benzamide, 1. To a solution of 4-aminophenol dissolved in NMP ( $-5^{\circ}\text{C}$ ), the fluorobenzoyl chloride was added dropwise over a 1 h period. The

reaction mixture was precipitated in cold water and filtered. Recrystallization from a chloroform/methanol solvent mixture gave **1** as a white crystalline solid: mp = 237-238 °C. The spectral properties and elemental analysis agreed with the assigned structure. Anal. Calcd. for C<sub>13</sub>H<sub>10</sub>FNO: C, 67.53; H, 4.33; N, 6.06. Found: C, 67.17; H, 4.32; N, 6.10.

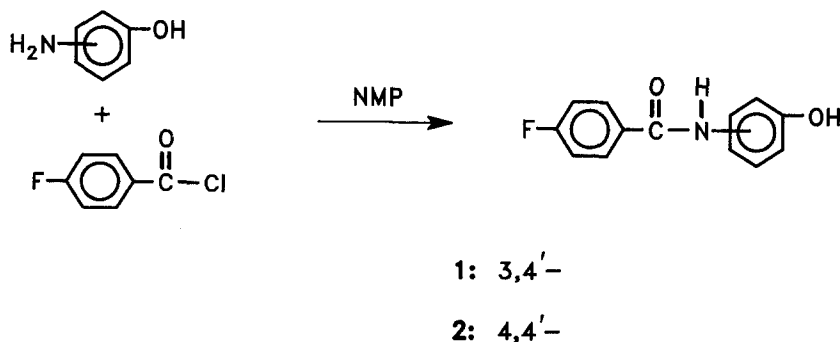
4-Fluoro-N-(3-hydroxyphenyl)benzamide, **2**. Monomer **2** was prepared using the procedure described above. Recrystallization of from chloroform gave **2** as a white powder: mp = 173-174 °C. Anal. Calcd. for C<sub>13</sub>H<sub>10</sub>FNO: C, 67.53; H, 4.33; N, 6.06. Found: C, 67.58; H, 4.41; N, 6.06.

### Polymerizations

The 4-fluoro-N-(4-hydroxyphenyl)benzamide and K<sub>2</sub>CO<sub>3</sub> were charged in a three necked flask, equipped with a Dean-Stark trap, a condenser and a stirrer, and rinsed in with an NMP/CHP solvent mixture. During the initial stage of polymerization, the reaction was maintained at 150 °C and the water generated by phenoxide formation was removed through the Dean Stark trap. After complete dehydration the temperature was increased to 180-190 °C to effect the displacement reaction. The resulting polymer was precipitated in excess of water/methanol, washed with water and dried under vacuum. The 4-fluoro-N-(3-hydroxyphenyl)benzamide was also subjected to self-polymerization according to the procedure mentioned above.

### Results and Discussion

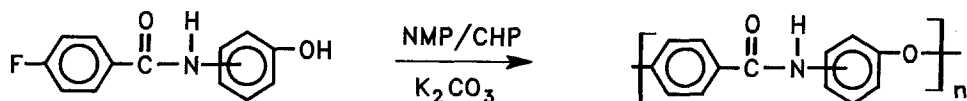
In order to demonstrate the plausibility of the amide-activated fluoro-displacement to prepare high molecular weight poly(aryl ether amides), the appropriate A-B monomers were prepared. The synthesis of 4-fluoro-N-(4-hydroxyphenyl)benzamide, **1**, and 4-fluoro-N-(3-hydroxyphenyl)benzamide, **2**, involved the reaction of 4-fluorobenzoyl chloride with either 4- or 3- aminophenol, respectively, in NMP (-5 °C) (Scheme 2). For each synthesis, quantitative conversion of starting material was observed with the formation of a single product peak (TLC). The resulting monomers were precipitated in water, isolated, and recrystallized to afford white crystalline powders with the predicted C, H and N values and the appropriate spectral characteristics.



Scheme 2

The self-polymerization of **1** or **2** was carried out in an NMP/CHP solvent mixture in the presence of K<sub>2</sub>CO<sub>3</sub> (Scheme 3). 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. Since CHP is not miscible with water

at temperatures above 100 °C, nonpolar cosolvents used to azeotrope the water generated during the polymerization were not required (3). The solids composition were maintained between 20 and 25 wt.% analogous to conventional poly(aryl ether) synthesis. The weak base  $K_2CO_3$  was used to form the reactive phenoxide since hydrolytic side reactions with the activated halide, typical of strong bases, are precluded. The water generated by phenoxide formation in the initial stages of the reaction were removed from the system due to the immiscibility with CHP and collected in the Dean-Stark trap (150 °C). Upon dehydration, the polymerization temperatures were increased to 180-190 °C to effect the hydrolytic aromatic displacement polymerization. High molecular weight polymers were obtained as judged by the dramatic increase in viscosities (24 h). The resulting polymers were filtered, coagulated in excess water/methanol, washed in boiling water (to remove remaining inorganic salts) and dried in vacuum oven to a constant weight. It is important to note that the stringent monomer delivery criteria, typical of most step growth polymerization to maintain proper stoichiometry, was not required in the self polymerization of either 1 or 2, since 1:1 stoichiometry is inherent to the monomer.



1: 1,3 -

3: derived from 1

2: 1,4 -

4: derived from 2

### Scheme 3

High molecular weight polymer was achieved for each of the A-B monomers (1 and 2) producing polymers 3 and 4, respectively. Table 1 contains the intrinsic viscosity measurements and thermal analysis for the poly(aryl ether amides). The intrinsic viscosity values of 3 and 4 were 0.50 and 1.45 dl/g, respectively, and considered high for a poly(aryl ether). For comparison, the commercially available poly(aryl ether sulfone) has an intrinsic viscosity of 0.48 dl/g in NMP. Polymer 3 was soluble in NMP and other aprotic dipolar solvents, consistent with the introduction of the aryl ether linkages. However, polymer 4 was only marginally soluble in NMP after isolation, typical of a conventional aromatic polyamide. Polymer 3 showed a high Tg (Table 1), consistent with the values of other rigid poly(aryl ethers). However, the calorimetry measurements showed no Tg for 4. It is important to note that bridging effects, typical of many A-B monomers for poly(ether) syntheses, were not observed for either of the A-B monomers (5,7).

Table 1  
Characteristics of Poly(Aryl Ether Amides)

Sample Entry	$(\eta)_{25^\circ C}^{NMP}$ dl/g	Tg, °C
3	0.5	225
4	1.45	—

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