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# Linear Poly(arylene ether)s with Pendant Benzoyl Groups: Geometric Isomers of PEEK or Substituted Poly(phenylene oxide)?

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ABSTRACT: The characterization and nucleophilic aromatic substitution (NAS) behavior of 3,5-difluorobenzophenone, **5**, are reported. The reactivity of the electrophilic sites, activated by only a benzoyl group located in the *meta* position, in **5** was probed via NMR spectroscopy and model reactions and was determined to be sufficient to undergo typical NAS reactions. Displacement of the first fluoride atom in **5**, with the phenoxide ion derived from *p*-cresol, required a reaction temperature of 150 °C for 21 h and resulted in a significant decrease in reactivity for displacement of the second fluoride atom, which required 185 °C for displacement. Confirmation that the displacement reaction of both fluorides occurred via an $S_NAr$ mechanism was provided by $^1H$ and $^{13}C$ NMR data on the model compounds. High molecular weight, amorphous poly(arylene ether)s, bearing a pendant benzoyl group, were prepared via the reaction of **5** with a variety of bis-phenols under typical NAS conditions. The glass transition temperatures ($T_g$) ranged from 111 to 133 °C while the 5% weight loss temperatures ranged from 488 to 494 °C under nitrogen and from 438 to 482 °C in air.

## Introduction

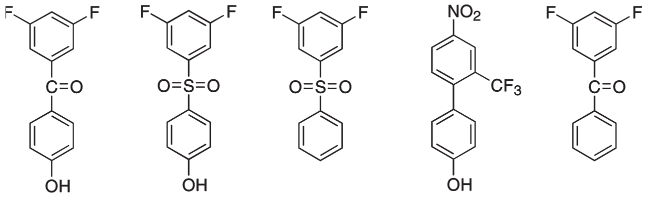
The synthesis of poly(arylene ether)s, PAEs, is typically achieved through nucleophilic aromatic substitution (NAS) reactions[1,2] of activated aryl halides with phenolate ions. A wide variety of activating groups have been employed such as the strongly electron-withdrawing sulfonyl,[2−6] carbonyl,[7−9] and phosphoryl groups.[10−15] However, a number of groups that do not possess very strong electron-withdrawing capabilities, including azomethine,[16] thianthrene,[17] benzoxazole,[18,19] phenylquinoxaline,[20−24] benzimidazole,[25] triazole,[26] and sulfide,[27] have been successfully utilized as the activating group in the synthesis of poly(arylene ether)s. In all of these cases, the activating group is located in the *para* position relative to the aryl halide and activates the electrophilic position by decreasing the electron density at the *ipso* carbon atom. The activating group also serves to stabilize the anionic intermediate, the Meisenheimer complex. In principle, a very strong electron-withdrawing group may provide sufficient activation to allow NAS to occur in the *meta* position; however, there are very few examples of this concept being utilized to prepare polymeric materials (see Figure 1).

The synthesis of hyperbranched poly(ether ketone)s via NAS reactions of 4-hydroxy-3′,5′-difluorobenzophenone, **1**, has been reported by Hawker and Chu.[28] Hyperbranched poly(arylene ether sulfone)s have also been prepared from 4-hydroxy-3′,5′-difluorophenyl sulfone, **2**.[29] In both of these systems relatively high molecular weight hyperbranched PAEs were achieved under typical NAS conditions. However, the synthesis of hyperbranched polymers does not require the quantitative displacement of both aryl fluorides as would be required to prepare their high molecular weight linear analogues. Kaiti et al. have recently reported the synthesis of high molecular weight PAEs bearing a pendant phenylsulfonyl group by utilizing 3,5-difluorodiphenyl sulfone, **3**, proving the feasibility of preparing PAEs from *meta* activated monomers.[30] In related work, Kim et al. reported the synthesis of poly(arylene ether)s from a biphenyl monomer, 4′-hydroxy-3-trifluoromethyl-4-nitrobiphenyl, **4**, in which the nitro group was sufficiently activated for displacement, by the trifluoromethyl group located in the *meta* position, to afford relatively high molecular weight PAEs.[31] We now wish to report on our studies of the NAS behavior of 3,5-difluorobenzophenone, **5**, and its subsequent application to prepare high molecular weight PAEs bearing pendant benzoyl groups which can be considered either geometric isomers of poly(ether ether ketone), PEEK, or functionalized poly(phenylene oxide)s, PPO.

## Experimental Section

All reactions were performed under a nitrogen atmosphere, and all transfers were done using syringes or cannula as necessary. *N*-Methylpyrrolidinone and dimethyl sulfoxide were dried over $CaH_2$ and distilled under a nitrogen atmosphere prior to use. 3,5-Difluorobenzophenone, **5**, was purchased from Alfa Aesar and was recrystallized from ethanol and dried in vacuo prior to use. $^1H$ and $^{13}C$ NMR spectra were obtained using a Bruker AVANCE 300 MHz instrument operating at 300 and 75.5 MHz, respectively. $^{19}F$ NMR spectra were obtained using a Bruker Avance 400 MHz instrument operating at 376.5 MHz using 10% $CFCl_3$ as an external standard with the instrument set relative to the lock signal. Samples were dissolved in dimethyl-$d_6$ sulfoxide or chloroform-$d$ as required. SEC analysis was performed using a Viscotek Model 300 TDA system equipped with refractive index, viscosity, and light scattering detectors operating at 70 °C. Two Polymer Laboratories 5 μm PL gel Mixed C columns were used with NMP (with 0.5% LiBr) as the eluent and a Thermoseparation Model P1000 pump operating at 0.8 mL/min. Polymer molecular weights were calculated from the RI signal and are reported relative to polystyrene standards. DSC and TGA analyses were performed under nitrogen and air atmospheres on a TA Instruments Q200 DSC and a TA Instruments Q500 TGA, respectively, at a heating rate of 10 °C/min.

**Monosubstituted Model Compound, 6a.** In a 100 mL RB flask equipped with a stir bar, condenser, and a gas adapter were placed 0.5 g (23 mmol) of **5**, 0.239 g (23 mmol) of *p*-cresol, 0.476 g (1.5 equiv) of $K_2CO_3$, and 3.48 mL of NMP (0.66 M). The flask was immersed in an oil bath and heated to 150 °C for 22 h, at which point the reaction mixture was cooled to room temperature and added dropwise into a large excess of water



**1** **2** **3** **4** **5**

**Figure 1.** Structures of monomers possessing aryl fluorides that are activated toward NAS reactions by electron-withdrawing groups located in *meta* positions.

**Table 1. Comparison of $^{13}$C and $^{19}$F NMR Chemical Shifts and Calculated Natural Charges for a Series of $B_2$ Monomers Utilized for NAS to Those for 5**

| compound | $^{13}$C ($\delta$)[b] | $^{19}$F ($\delta$)[c] |
|---|---|---|
| 4,4′-difluorophenyl sulfone[a] | 165.31 | −104.08 |
| bis(4-fluorophenyl)methanone[a] | 165.27 | −106.01 |
| bis(4-fluorophenyl)phenyl phosphine oxide[a] | 165.05 | −106.71 |
| 2,3-diphenyl-6-fluoroquinoxaline[a] | 164.8 | −107.81 |
| 3,5-difluorophenylsulfone, **3** | 162.9 | −106.32 |
| 3,5-difluorobenzophenone, **5** | 162.8 | −109.3 |
| monosubstituted model compound, **6a** | 163.8 | −110.6 |

[a] Data taken from ref32. [b] Data acquired in $CDCl_3$. [c] Data acquired in DMSO-$d_6$.

**Table 2. Percent Yield, Molecular Weight, and Polydispersity Data for Poly(arylene ether)s Prepared from 5 under Various Conditions ($M_n$ Values Are Reported Relative to Polystyrene Standards)**

| polymer | $A_2$[a] | solvent[b] | time (h) | yield (%) | $M_n$ (Da) | PDI |
|---|---|---|---|---|---|---|
| **8a** | **7a** | NMP | 18 | 66 | 34 100 | 5.9 |
| **8b** | **7b** | NMP | 18 | 64 | 7 300 | 1.5 |
| **8c** | **7c** | NMP | 18 | 70 | 54 200 | 5.4 |
| **8d** | **7d** | NMP | 18 | 64 | 12 200 | 2.3 |

[a] Concentrations of **5** and $A_2$ were 0.64 M. [b] All reactions were performed with a final oil bath temperature of 185 °C.

(400 mL) at pH = 4.0. The resulting off-white solid was extracted into chloroform and washed repeatedly with water. The chloroform layer was dried overnight over $MgSO_4$, and the solvent was removed with use of rotary evaporator and vacuum to afford 0.51 g (73%) of **6a** (along with residual **5** and **6b**) as an oil. $^1$H NMR ($CDCl_3$, $\delta$): 2.36 (s, 3H); 6.88 (dt, 1H); 6.99 (d, 2H); 7.09 (d, 2H); 7.20 (m, 2H); 7.33 (dt, 1H); 7.49 (m, 2H); 7.61 (tt, 1H); 7.82 (d, 1H). $^{13}$C NMR ($CDCl_3$, $\delta$): 21.0 (s); 109.1 (d); 111.1 (d); 115.1 (s); 120.1 (s); 128.7 (s); 130.2 (s); 130.9 (s); 133.1 (s); 136.7 (s); 137.0 (s); 140.6 (s); 153.5 (s); 159.8 (d); 163.2 (d); 194.9 (s). $^{19}$F NMR (DMSO-$d_6$, $\delta$): −110.60.

**Disubstituted Model Compound, 6b.** In a 25 mL RB flask equipped with a stir bar, condenser, and a gas adapter were placed 0.22 g (10 mmol) of **5**, 0.208 g (20 mmol) of *p*-cresol, 0.345 g (2.5 equiv) of $K_2CO_3$, and 3.0 mL of NMP (0.33M). The flask was immersed in an oil bath and heated to 150 °C for 7.5 h, at which point GC/MS of a small sample showed $\sim$90% conversion to **6a**. The oil bath temperature was then raised to 185 °C for an additional 18 h. The reaction mixture was cooled to room temperature and slowly poured into a large excess of water (400 mL). The resulting off-white solid was extracted into ether and washed repeatedly with water. The ether layer was dried over $MgSO_4$, and the solvent was removed to afford 0.31 g (76%) of **6b** as an oil. $^1$H NMR ($CDCl_3$, $\delta$): 2.32 (s, 6H); 6.85 (t, 1H); 6.96 (d, 4H); 7.07 (d, 2H); 7.16 (d, 4H); 7.46 (t, 2H); 7.57 (tt, 1H); 7.80 (dd, 2H); $^{13}$C NMR ($CDCl_3$, $\delta$): 21.1 (s); 111.9 (s); 113.7 (s); 119.6 (s); 128.5 (s); 130.2 (s); 130.6 (s); 132.9 (s); 134.0 (s); 137.2 (s); 140.2 (s); 153.9 (s); 159.3 (s); 195.6 (s).

**Typical Polymerization Procedure, 8d.** In a 25 mL RB flask equipped with a stir bar, Dean−Stark trap, condenser, and gas adapter were placed 0.5 g (23 mmol) of **5**, 0.428 g (23 mmol) of **7d**, 0.791 g (1.5 equiv) of $K_2CO_3$, 3.48 mL of NMP, and 3.48 mL of toluene. The Dean−Stark trap was filled with toluene, and the mixture was heated to 145 °C for approximately 3−4 h to ensure complete dryness. The toluene was removed, and the reaction temperature was raised to 185 °C for an additional 18 h, at which point the mixture was cooled to room temperature and slowly poured into 400 mL of vigorously stirred acidic water to precipitate the polymer as a slightly colored, purple, fibrous solid which was redissolved in THF and was added dropwise to 400 mL of vigorously stirred methanol to precipitate a white powder that was isolated via filtration and dried in vacuo to afford 0.55 g of **8d** (66%). $^1$H NMR ($CDCl_3$, $\delta$): 6.99 (t, 1H); 7.13 (d, 4H); 7.17 (d, 4H); 7.47 (m, 1H); 7.57 (m, 6H); 7.84 (d, 2H). $^{13}$C NMR ($CDCl_3$, $\delta$): 112.9, 114.7, 119.9, 122.1, 128.7, 130.3, 133.1, 136.7, 137.2, 140.7, 154.6, 158.9, 195.5.

All subsequent polymerization reactions were performed under similar conditions which included an azeotropic drying period of 3−4 h, followed by removal of the toluene and heating to 185 °C. The total reaction times, for each $A_2$ monomer, are listed in Table 2.

**8a** (66%). $^1$H NMR ($CDCl_3$, $\delta$): 1.65 (s, 6H); 6.90 (t,1H); 6.94 (d, 4H); 7.07 (d, 2H); 7.19 (d, 4H); 7.41 (t, 2H); 7.52 (t, 1H); 7.75 (d, 2H). $^{13}$C NMR ($CDCl_3$, $\delta$): 31.2, 42.4, 112.6, 114.2, 119.0, 128.3, 130.2, 132.8, 137.2, 140.2, 146.5, 154.2, 159.0, 195.4.

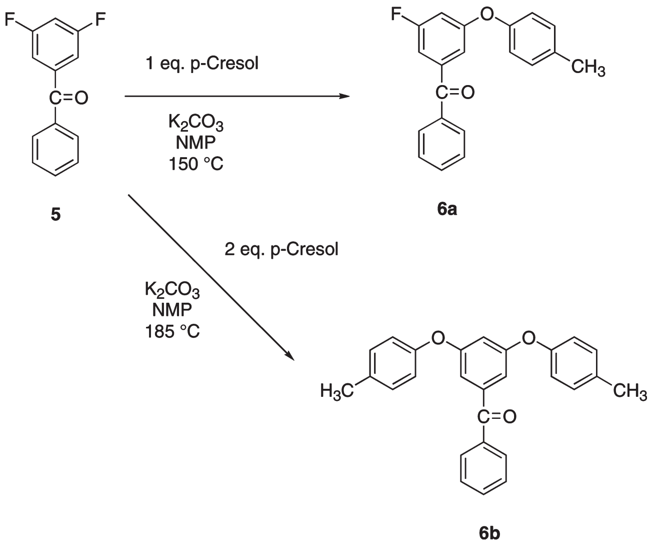
**8b** (64%). $^1$H NMR ($CDCl_3$, $\delta$): 6.89 (t, 1H); 6.99 (d, 4H); 7.35 (d, 2H); 7.39 (d, 4H); 7.51 (m, 2 H); 7.61 (m, 1H); 7.89 (d, 2 H). $^{13}$C NMR ($CDCl_3$, $\delta$): 63.81 (heptet, $C(CF_3)_2$), 114.5, 115.4, 116.1, 118.4 (q, $CF_3$), 122.4, 126.2, 128.7, 130.2, 132.1, 133.1, 136.9, 140.7, 157.1, 157.7, 195.1.

**8c** (70%). $^1$H NMR ($CDCl_3$, $\delta$): 6.74 (t, 1H); 6.98 (m, 8H); 7.17 (d, 2H); 7.56 (m, 2H); 7.59 (m, 1 H); 7.87 (d, 2H). $^{13}$C NMR ($CDCl_3$, $\delta$): 111.4, 113.5, 119.9, 121.3, 128.5, 130.2, 133.0, 137.1, 140.3, 151.6, 154.0, 159.4, 195.4.

## Results and Discussion

A number of authors have employed $^{13}$C and $^{19}$F NMR spectroscopy to probe the reactivity of electrophilic sites in aromatic halides.[32,17,20,33] Carter reported an extensive study regarding the NAS polymerization reactions of a wide variety of aryl difluoride monomers and determined that *ipso* carbon atoms with decreased electron density, correlating with an increase in reactivity toward NAS, displayed $^{13}$C NMR chemical shifts that were considerably downfield relative to those with higher electron density.[32] Similar trends were observed with $^{19}$F NMR chemical shifts, and the wider chemical shift range observed for $^{19}$F NMR seemed to provide a more reliable gauge of the potential for NAS reactions. The $^{13}$C and $^{19}$F NMR chemical shift data for a selected series of aryl difluoride monomers, as well as that for **5**, are listed in Table 1. A comparison of the data for **5** with that for a series of $B_2$-type monomers, which readily undergo NAS to form poly(arylene ether)s, indicate that the electrophilic sites in **5** are sufficiently activated to undergo NAS reactions under relatively mild conditions. It is interesting to note that the $^{13}$C chemical shifts indicate that the benzoyl group in **5** is nearly as activating when compared to the phenylsulfonyl group in **3**, which also provides activation of the aryl fluorides through inductive effects alone rather than any direct resonance effect. In contrast, the $^{19}$F NMR chemical shifts for **3** and **5** (−106.32 and −109.3, respectively) indicate that the activating effect of the benzoyl group in the *meta* position is considerably weaker than the phenyl sulfonyl group in the same position. The same level of discrepancy in chemical shift data is observed with 4,4′-difluorophenyl sulfone and bis(4-fluorophenyl)methanone in which the $^{13}$C NMR chemical shift data are nearly identical, but the $^{19}$F NMR data indicate that the ketone is considerably less reactive than the sulfone. In fact, it

Scheme 1



was determined experimentally that the sulfone monomer was ~6 times as reactive as the ketone.[32]

**Model Reactions.** The experimental reactivity and mechanism of fluoride displacement in **5** were probed via model reactions as outlined in Scheme 1. The phenoxide derivative of *p*-cresol was chosen as the nucleophile for the model reactions because its nucleophilic strength should very closely mimic that of bisphenol A. Reaction of 1 equiv of *p*-cresol with **5** at 150 °C in NMP for 22 h afforded a product mixture consisting of ~6.7% of **5**, 89.8% of **6a**, and 3.4% of **6b** as determined by GC/MS as well as $^1$H and $^{19}$F NMR spectroscopy. If the two electrophilic sites in **5** were of equal reactivity, a statistical product ratio of 25:50:25 (**5**:**6a**:**6b**) would have been observed. These results indicated a significant decrease in the reactivity of the electrophilic site in **6a** compared to those in **5**.

Further evidence for a decrease in reactivity on going from **5** to **6a** was gleaned from the reaction of 2 equiv of *p*-cresol with **5**, which required a temperature of 185 °C to reach ~100% completion and afford **6b** in the same 18 h reaction time. The $^{19}$F NMR data (Table 1) also confirmed the decrease in reactivity on converting **5** to **6a** as the $^{19}$F NMR chemical shift of **6a** was $-110.6$ ppm vs $-109.3$ ppm for **5**, indicating a significant increase in the electron density present at the electrophilic site in **6a**. Ironically, the $^{13}$C NMR chemical shift data for **6a** and **5** indicate that the reactivity of the second fluorine for displacement actually increases; however, this is in stark contrast to the observed product ratio for the 1:1 reaction and the elevated temperatures required to displace the second fluorine atom. This apparent contradiction between $^{13}$C and $^{19}$F NMR chemical shifts in terms of their use for predicting reactivity in NAS reactions lends further credence to the use of $^{19}$F NMR spectroscopy as the preferred methodology. Even though a significant decrease in the reactivity of **6a** was observed, both experimentally and in $^{19}$F NMR spectroscopic data, the second displacement proceeded under relatively mild conditions, 185 °C, to afford **6b** in quantitative yield ($^1$H NMR spectroscopy and GC/MS of a sample indicated complete conversion to **6b**), thus indicating a sufficient level of reactivity to prepare high molecular weight PAEs.

**Mechanistic Evidence.** Confirmation that the model reactions proceeded via a typical $S_NAr$ mechanism, rather than a benzyne mechanism, is provided by $^1$H and $^{13}$C NMR spectroscopic analysis (Figures 2 and 3, respectively). In the $^1$H NMR spectrum of **5**, the signal assigned to proton *e* appears as a triplet of triplets (boxed in regions). The same signal appears as a doublet of doublet of doublets (appearing as a doublet of triplets) and a triplet in **6a** and **6b**, respectively. If a benzyne mechanism was operating, the molecular symmetry would be disrupted and the clean triplets would not be observed. The same conclusion was reached by analysis of the $^{13}$C NMR spectra of **5**, **6a**, and **6b** (Figure 3).

The key step in NAS reactions is the addition of the nucleophile to the *ipso* carbon atom, which results in the formation of a relatively stable Meisenheimer complex. Although the carbonyl moiety does not provide any stabilization via a direct resonance pathway (Scheme 2), a number of resonance forms can be drawn for the intermediate in which the anion is adjacent to either a strongly electron-withdrawing fluorine or the electron-withdrawing carbonyl group. In the second fluorine displacement, the stabilization afforded by the fluorine atom is absent, and the intermediate is presumed to be considerably less stable which requires a higher reaction temperature. However, it is readily apparent from the model reactions that the stabilization provided via inductive effects is sufficient to permit a *typical* NAS process to occur.

**Polymerization Reactions.** Polymerization reactions of **5** with a variety of bis-phenol monomers were carried out under typical NAS conditions, as outlined in Scheme 3. After an initial precipitation from water, the polymers were redissolved in THF and precipitated again from methanol, in order to remove any low molecular weight byproducts, before analysis. The percentage yield, molecular weight, and polydispersity data as determined by SEC analysis are listed in Table 2.

The percentage yields, upon precipitation from methanol, ranged from 64 to 70%, indicating that a significant amount of low molecular weight material remained soluble in the methanol. The $M_n$ values of the samples, with the exception of the Bis-AF polymer, **8b**, were well above 10 000 Da. For example, the $M_n$ value of **8a** was 34 100 Da with a PDI of 5.9 while the $M_n$ value for **8c** was 54 200 Da with a PDI value of 2.3.

It was important to determine if the same $S_NAr$ mechanism was operating in the polymer forming reaction as was observed in the model reactions. Figures 2d and 3d display the aromatic regions of the $^1$H and $^{13}$C NMR spectra of **8d**. As was the case in the model reactions, the signal assigned to proton *e* in **5** appears as a triplet in **8d**, thus confirming that no change in reaction mechanism occurred under the polymerization conditions. Further evidence for this conclusion was derived from analysis of the $^{13}$C NMR spectrum of **8d,** which displayed only one signal for the carbon atoms in the new C−O bonds as well as the carbon atom adjacent to the C=O group.

**Thermal Analysis.** The thermal properties of **8a**−**8d** were investigated via DSC and TGA, and the data are listed in Table 3. DSC analysis showed that all of the samples were completely amorphous with only glass transition temperatures, $T_g$, being observed in DSC traces up to 400 °C (see Figure 4). The polymer prepared with **7c** displayed the lowest $T_g$ value, 111 °C, while the more rigid **7d** afforded a PAE sample with a $T_g$ of 126 °C. Somewhat surprisingly, the polymer prepared from Bis-AF, **7b**, possessed the highest $T_g$ value, 133 °C. All of the $T_g$'s observed for **8a**−**8d** were significantly lower (15−50 °C) than the corresponding PAEs prepared from the sulfone analogue, **3**. In part, this observation may be due to weaker intermolecular forces present with the benzoyl group compared to the phenylsulfonyl group. In addition, the smaller bond angle, C−S−C ~ 102° for the sulfonyl group in **3** versus ~120° for

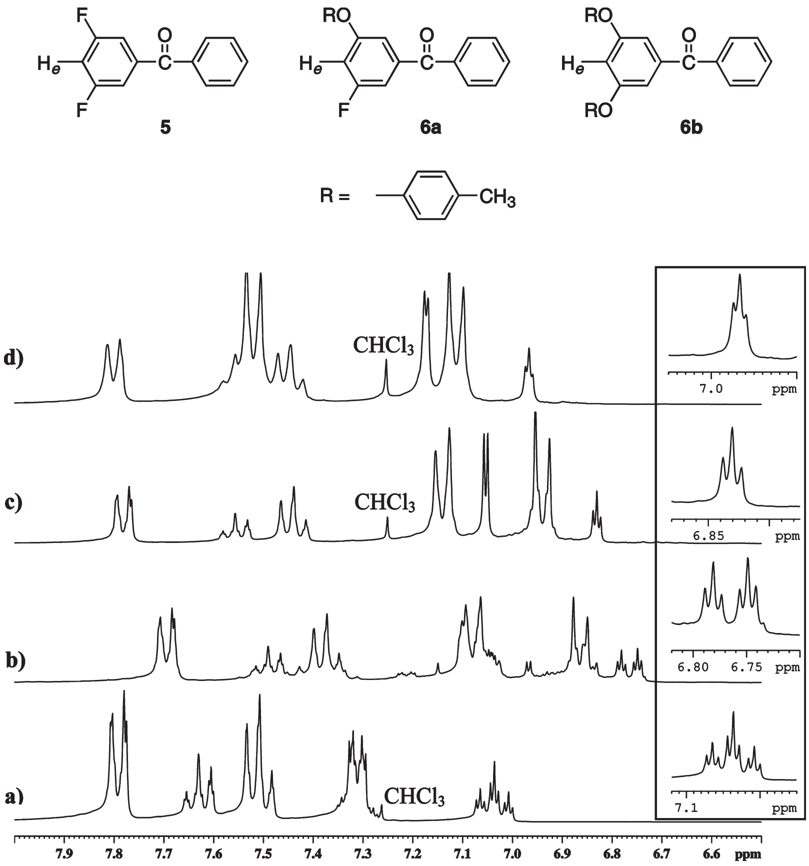


**Figure 2.** Aromatic regions of the 300 MHz $^1$H NMR spectra (CDCl$_3$) of (a) **5**, (b) **6a**, (c) **6b**, and (d) **8d**. The signals assigned to proton *e* in **5**, **6a**, **6b**, and **8d** are highlighted in the box.

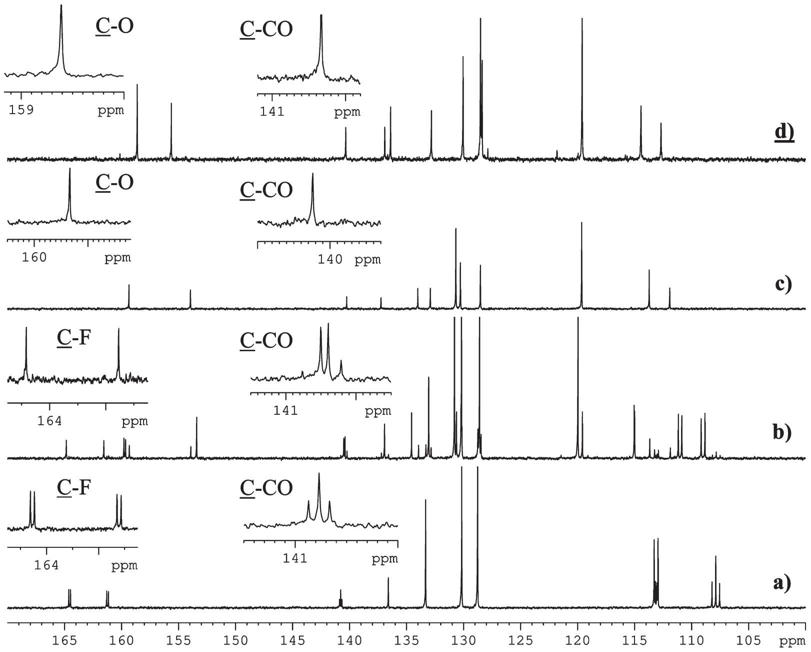
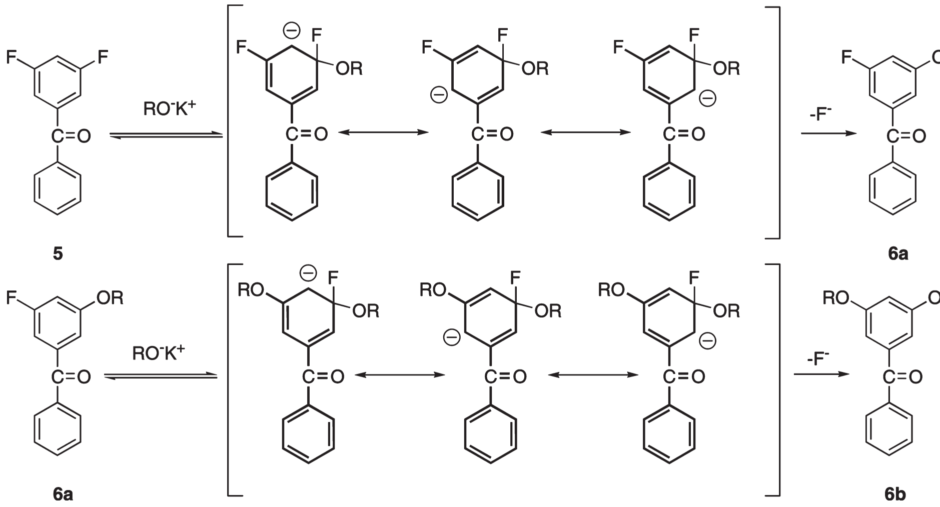


**Figure 3.** Aromatic regions of the 75.5 MHz $^{13}$C NMR spectra (CDCl$_3$) of (a) **5**, (b) **6a**, (c) **6b**, and (d) **8d**.

benzoyl group in **5** might result in a higher barrier for bond rotation in the main chain, although it is difficult to decouple these two effects.

From a structural standpoint the backbones of polymers **8a**−**8d** are analogous to poly(phenylene oxide),[35] PPO, but carry a pendant benzoyl group. However, their overall composition more closely relates to poly(ether ether ketone), PEEK, and it various derivatives. In fact, polymer **8c** is simply the geometric isomer of poly(ether ether ether ketone), PEEEK.[34] Figure 6 depicts a number of PPO and PEEK structures, as well as **8c**, and their associated thermal transition temperatures. The influence of the presence of *meta* (1,3) phenylene units on the crystallinity in these systems is readily apparent. For example, poly(ether ketone), Scheme 2



Scheme 3

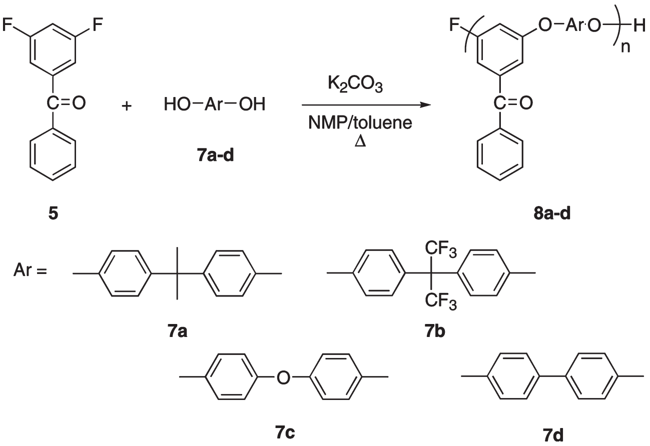


**Table 3. Thermal Analysis Data for Poly(arylene ether)s Prepared from 5 and a Series of Bis-Phenol Monomers**

| polymer | $T_g$ (°C) | $T_{d(5\%)}$ $N_2$ (°C) | $T_{d(10\%)}$ $N_2$ (°C) | $T_{d(5\%)}$ air (°C) | $T_{d(10\%)}$ air (°C) |
|---|---|---|---|---|---|
| **8a** | 119 | 494 | 504 | 438 | 481 |
| **8b** | 133 | 491 | 515 | 477 | 509 |
| **8c** | 111 | 489 | 523 | 451 | 481 |
| **8d** | 126 | 488 | 541 | 482 | 541 |

PEK, is a highly crystalline material with a melting temperature, $T_m$, of 366 °C, *iso*-PEK (*meta*) is completely amorphous, and the corresponding copolymer with *meta* and *para* links is semicrystalline with a $T_m$ of 193 °C.[8] Similar trends are observed with PPO derivatives as an increase in *meta* units disrupts crystallinity, leading to a lower $T_m$.[36]

The most direct comparison of the thermal properties of **8a**–**8d** can be made with **8c**, PEEEK,[34] and PPO-4*p*/1*m*.[36] The backbone of **8c** consists of two *para* phenyl ethers and one *meta* phenylene ether unit, PEEEK consists of only *para* phenylene ether units and one *para* benzophenone unit, and PPO-4*p*/1*m* possesses *para* and *meta* phenylene ether units in a ratio of 4:1. Both PEEEK and PPO-4*p*/1*m* are sufficiently crystalline to display a $T_m$, but **8c** appears to be completely amorphous. The amorphous nature of **8c** indicates a lowered ability for close-chain packing which may be caused by either the pendant benzoyl group or the disruption in symmetry caused by the lowered *para* to *meta* phenylene ether ratio (relative to PPO-4*p*/1*m*) or both effects. Regardless, **8c**, as well as the other new materials, **8a**, **8b**, and **8d**, represent hybrid structures which combine elements of PEEKs and PPOs.

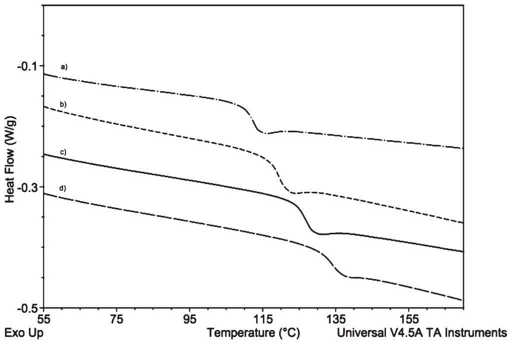


**Figure 4.** DSC traces for polymers **8a**–**8d** in nitrogen at a heating rate of 10 °C/min: (a) **8c**, (b) **8a**, (c) **8d**, and (d) **8b**.

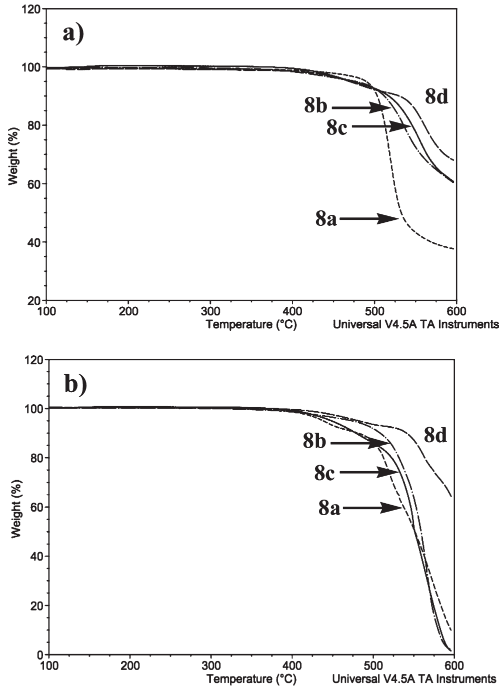


**Figure 5.** TGA thermograms for polymers **8a**–**8d** in (a) nitrogen and (b) air at a heating rate of 10 °C/min.

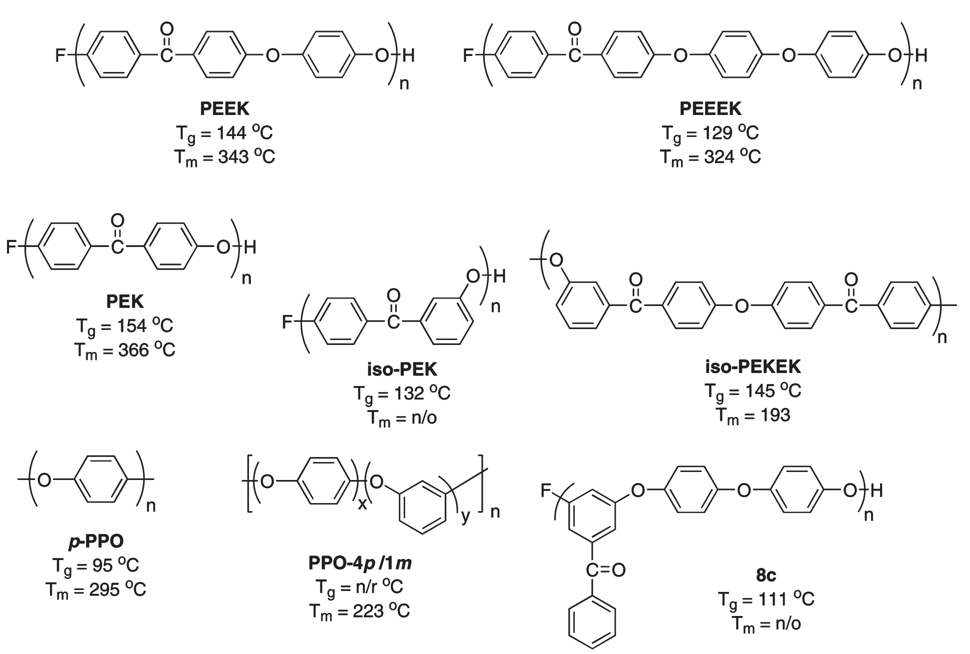


**Figure 6.** Structures and thermal data (taken from reference given) for a variety of poly(arylene ether)s including poly(ether ether ketone), PEEK,[8] poly(ether ether ether ketone), PEEEK,[34] poly(ether ketone), PEK,[8] isomeric forms of PEK (*iso*-PEK[8] and *iso*-PEKEK[8]), poly(phenylene oxide)s, PPO,[35] isomeric PPO-4*p*/1*m* (4 *para* links and 1 *meta* link[36]), and polymer **8c** (geometric isomer of PEEEK) (n/o = not observed; n/r = not reported).

The thermal stability of **8a**−**8d** was evaluated under nitrogen and air atmospheres (Figure 5). At a heating rate of 10 °C/min, under nitrogen, sample **8a**, the fluorinated sample **8b**, and the most aromatic sample, **8d**, possessed 5% weight loss temperatures of 494, 491, and 488 °C, respectively. In air, the corresponding values for **8a**, **8b**, and **8d** were 438, 477, and 482 °C, respectively. These results indicate that, although these new materials are completely amorphous, they possess excellent thermal stability. The added thermal stability may, in part, be derived from the absence of a strongly electron-withdrawing group in the backbone of these new systems.

## Conclusions

A new $B_2$ monomer, **5**, in which the activating group for nucleophilic aromatic substitution is located in the *meta* position has been evaluated as a route to poly(arylene ether)s with pendant benzoyl groups. The $^{19}F$ NMR chemical shift of the fluorine atoms in **5**, −109.3. ppm, indicated that the electrophilic sites were sufficiently activated to undergo a nucleophilic aromatic substitution reaction. Displacement of the first fluoride atom in **5**, with the phenoxide ion derived from *p*-cresol, was achieved in as little as 6−7 h at 150 °C while displacement of the second fluoride atom required 185 °C to reach completion in 22 h. These significantly different reaction temperatures indicated a substantial decrease in reactivity of the second electrophilic site, which was confirmed by an upfield shift of ~1.4 ppm in the $^{19}F$ NMR spectrum of **6a**. Confirmation that the fluoride displacement reactions in **5** proceeded via an $S_NAr$ mechanism was provided by $^1H$ and $^{13}C$ NMR data of model compounds and polymer samples. Amorphous poly(arylene ether)s, bearing a pendant benzoyl group, were prepared via the reaction of **5** with a variety of bis-phenols under typical NAS conditions. Number-average molecular weights, after removal of oligomeric species, ranged from 7300 Da, with Bis-AF, to 54 200 Da, with 4,4′-dihydroxydiphenyl ether. The poly(arylene ether)s possessed relatively low glass transition temperatures ($T_g$) which ranged from 111 to 133 °C but displayed excellent thermal stability with the 5% weight loss temperatures ranging from 438 and 494 °C, with bisphenol A, to 488 and 489 °C, with 4,4′-dihydroxybiphenyl, under air and nitrogen, respectively. Utilization of **5** as a platform to prepare linear poly(arylene ether)s carrying a variety of pendant groups is currently being investigated.

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