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Linear Poly(arylene ether)s with Pendant Phenylsulfonyl Groups: Nucleophilic Aromatic Substitution Activated from the Meta Position

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ABSTRACT: The synthesis, characterization, and nucleophilic aromatic substitution (NAS) behavior of 3,5-difluorophenyl sulfone, **3**, are reported. The reactivity of the electrophilic sites, activated by only a phenylsulfonyl group located in the meta position, in **3** was probed via NMR spectroscopy and model reactions and was determined to be sufficient to undergo NAS reactions. Displacement of the first fluoride atom in **3**, with the phenoxide ion derived from *p*-cresol, resulted in a significant decrease in reactivity for displacement of the second fluoride atom, however, not to such an extent as to prevent its displacement under more vigorous conditions. Confirmation of 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 phenylsulfonyl group, were prepared via the reaction of **3** with a variety of bisphenols under typical NAS conditions. The glass transition temperatures (T_g) ranged from 136 to 175 °C while the 10% weight loss temperatures ranged from 530 to 590 °C under nitrogen and from 507 to 562 °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,[2−4] carbonyl,[5,6] and phosphoryl groups.[7−12] However, a number of groups that do not possess very strong electron-withdrawing capabilities, including azomethine,[13] thianthrene,[14] benzoxazole,[15,16] phenylquinoxaline,[17−21] benzimidazole,[22] and triazole,[23] 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.

The synthesis of hyperbranched poly(ether ketone)s via NAS reactions of 4-hydroxy-3′,5′-difluorobenzophenone has been reported by Hawker and Chu.[24] Hyperbranched poly(arylene ether sulfone)s have also been prepared from 4-hydroxy-3′,5′-difluorophenyl sulfone.[25] In both of these systems relatively high molecular weight hyperbranched poly(arylene ether)s were achieved under typical NAS conditions. However, to the best of our knowledge, there have been no reports describing the synthesis of linear poly(arylene ether)s from monomers in which the only activating species is present in the meta position. We now wish to report on our studies of the S_NAr behavior of 3,5-difluorophenyl sulfone, **3**, and its subsequent application to prepare high molecular weight poly(arylene ether)s, PAEs.

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. Benzenesulfonyl chloride was purchased from Aldrich and distilled under vacuum prior to use. 1-Bromo-3,5-difluorobenzene was purchased from Fluorochem and was used as received. ^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 Perkin-Elmer DSC 7 and a Perkin-Elmer TGA 7, respectively, at a heating rate of 10 °C/min.

Synthesis of 3,5-Difluorophenyl Sulfone, 3. In a 250 mL round-bottomed flask equipped with a stir bar, addition funnel, condenser, and gas inlet were placed 2.105 g (86.6 mmol) of Mg turnings and enough THF to cover the metal. A solution of 15.94 g (82.5 mmol) of 1-bromo-3,5-difluorobenzene and 50 mL of THF was added slowly to the stirred Mg at room temperature; upon complete addition, the reaction mixture was stirred and allowed to react for 4 h. The resulting solution of 3,5-difluorophenylmagnesium bromide was transferred to an addition funnel and added dropwise to a mixture of 13.87 g (78.6 mmol) of benzenesulfonyl chloride in 60 mL of THF at 0 °C. The reaction mixture was stirred overnight followed by heating to reflux for 2 h. The reaction mixture was then diluted in 500 mL of ethyl ether and transferred to a separatory funnel. The ether layer was washed with dilute HCl, distilled water, 5% $NaHCO_3$, and again with distilled H_2O. The ether layer was dried over $MgSO_4$, filtered, and then evaporated to dryness to afford a yellow solid which was recrystallized, first from ethanol/water and then from hexanes to obtain 14.0 g (70% yield) of **3** (mp 99−101 °C) as a yellow, crystalline solid. ^1H NMR ($CDCl_3$, δ): 7.00 (tt, 1H); 7.45 (m, 2H); 7.58 (d, 2H); 7.62 (m, 1H); 7.95 (d, 2H). ^{13}C NMR ($CDCl_3$, δ): 108.8 (t); 111.2 (d); 128.0 (s); 129.6 (s);

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Table 1. Comparison of ^{13}C and ^{19}F NMR Chemical Shifts for a Series of B_2 Monomers Utilized for NAS to Those for 3

compound	^{13}C (δ)[b]	^{19}F (δ)[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-difluorophenyl sulfone, **3**	162.9	−106.32
monosubstituted model compound, **4a**	163.2	−107.70

[a] Data taken from ref 26. [b] Data acquired in $CDCl_3$. [c] Data acquired in DMSO-d_6.

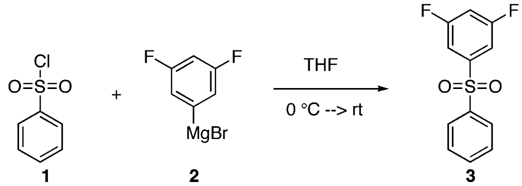
134.0 (s); 140.3 (s); 145.1 (t); 162.9 (dd). ^{19}F NMR (DMSO-d_6, δ): −106.32. Calcd Anal. for $C_{12}H_8F_2O_2S$: C, 56.69; H, 3.17. Found: C, 56.78; H, 3.31.

Monosubstituted Model Compound, 4a. In a 25 mL round-bottomed flask equipped with a stir bar, condenser, and a gas adapter were placed 0.500 g (1.97 mmol) of **3**, 0.213 g (1.97 mmol) of *p*-cresol, 0.408 g (1.5 equiv) of K_2CO_3, and 6.0 mL of NMP. The flask was immersed in an oil bath and heated to 75 °C for 21 h, at which point the reaction mixture was cooled to room temperature and slowly poured into a large excess of water (400 mL) at pH = 4.0. 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 0.56 g (84%) of **4a** (along with residual **3** and **4b**) as an off-white solid. ^{1}H NMR ($CDCl_3$, δ): 2.30 (s, 3H); 6.76 (ddd, 1H); 6.91 (d, 2H); 7.19 (d, 2H); 7.28 (dt, 1H); 7.33 (m, 1H); 7.54 (m, 2H); 7.63 (m, 1H); 7.96 (m, 2H). ^{13}C NMR ($CDCl_3$, δ): 20.82 (s); 108.9 (m); 112.0 (d); 120.0 (s); 127.5 (s); 128.5 (s); 130.0 (s); 133.0 (s); 134.5 (s); 140.5 (s); 144.4 (d); 152.0 (s); 160.5 (d); 163.2 (d). ^{19}F NMR (DMSO-d_6, δ): −107.70.

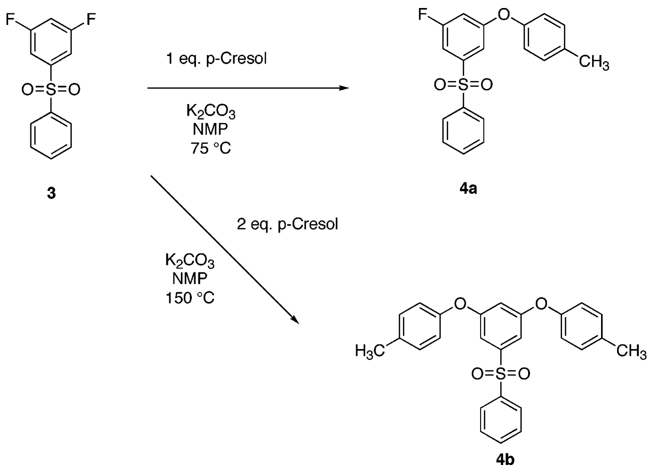
Disubstituted Model Compound, 4b. In a 25 mL round-bottomed flask equipped with a stir bar, condenser, and a gas adapter were placed 0.500 g (1.97 mmol) of **3**, 0.427 g (3.95 mmol) of *p*-cresol, 0.816 g (1.5 equiv) of K_2CO_3, and 6.0 mL of NMP. The flask was immersed in an oil bath and heated to 150 °C for 21 h, at which point ^{1}H NMR spectroscopy of a small sample showed complete conversion to **4b**. The reaction mixture was cooled to room temperature and slowly poured into a large excess of water (400 mL) at pH = 4.0. 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 0.72 g (85%) of **4b** as an off-white solid. ^{1}H NMR ($CDCl_3$, δ): 2.30 (s, 6H); 6.71 (t, 1H); 6.87 (d, 4H); 7.14 (m, 6H); 7.49 (m, 2H); 7.57 (m, 1H); 7.85 (m, 2H). ^{13}C NMR ($CDCl_3$, δ): 20.77 (s); 110.5 (s); 111.5 (s); 120.0 (s); 128.0 (s); 129.5 (s); 130.5 (s); 133.0 (s); 134.5 (s); 141.0 (s); 143.8 (s); 152.0 (s); 160.0 (s).

Typical Polymerization Procedure, 6a. In a 50 mL round-bottomed flask equipped with a stir bar, Dean Stark trap, condenser, and gas adapter were placed 1.00 g (3.94 mmol) of **3**, 0.899 g (3.94 mmol) of **5a**, 1.63 g (1.5 equiv) of K_2CO_3, 12 mL of NMP, and 12 mL of toluene. The Dean Stark trap was filled with toluene, and the mixture was heated to 165 °C for ∼3 h to ensure complete dryness. The toluene was removed, and the reaction temperature was raised to 185 °C for an additional 19 h, at which point the mixture was cooled to room temperature and slowly poured into 300 mL of vigorously stirred distilled water to precipitate the polymer as a brown, fibrous solid (1.57 g, 92 %). The fibrous solid was redissolved in THF, and methanol was slowly added to precipitate the polymer as a brown solid which was reprecipitated one additional time from THF/methanol as a white powder that was isolated via filtration and dried in vacuo to afford 1.11 g of **6a** (64%). ^{1}H NMR ($CDCl_3$, δ): 1.69 (s, 6 H); 6.77 (t, 1H); 6.90 (d, 4H); 7.20 (m, 6H); 7.49 (t, 2H); 7.59 (m, 1 H); 7.86 (d, 2H). ^{13}C NMR ($CDCl_3$, δ): 31.1, 42.4, 110.9, 112.2, 119.1, 127.7, 128.5, 129.3, 133.5, 141.0, 144.0, 146.9, 153.3, 159.6.

Scheme 1



Scheme 2



All subsequent polymerization reactions were performed under similar conditions which included an azeotropic drying period of 3 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.

6b (97%). ^{1}H NMR ($CDCl_3$, δ): 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 ($CDCl_3$, δ): 63.85 (heptet, $C(CF_3)_2$), 112.99, 114.05, 118.54, 124.08 (q, CF_3), 127.83, 129.10, 129.48, 132.12, 133.74, 140.63, 144.86, 156.36, 158.33.

6c (98%). ^{1}H NMR ($CDCl_3$, δ): 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 ($CDCl_3$, δ): 110.43, 111.43, 120.25, 121.37, 127.67, 129.38, 133.53, 141.10, 144.22, 150.82, 154.08, 160.17.

6d (96%). ^{1}H NMR ($CDCl_3$, δ): 6.87 (t, 1H); 7.08 (d, 4H); 7.29 (d, 2H); 7.54 (m, 7H); 7.90 (d, 2 H). ^{13}C NMR ($CDCl_3$, δ): 111.29, 112.53, 119.98, 127.80, 128.73, 129.40, 133.51, 136.87, 140.98, 144.36, 154.90, 159.49.

Table 2. Percent Yield, Molecular Weight, and Polydispersity Data for Poly(arylene ether)s Prepared from 3 under Various Conditions; M_n Values Are Reported Relative to Polystyrene Standards

				initial H_2O (ppt)			THF/methanol (ppt)		
	A_2[a]	solvent[b]	time (h)	% yield	M_n (Da)	PDI	% yield	M_n (Da)	PDI
6a	**5a**	NMP	22	92	8,800	10.9	64	31,200	3.90
6b	**5b**	NMP	7	97	5,760	10.9	66	39,900	2.19
6c	**5c**	NMP	7	98	5,790	48.9	64	118,000	4.17
6d	**5d**	NMP	6	96	4,270	36.7	70	50,500	4.27
6e	**5e**	NMP	7	95	2,120	6.33	70	11,200	2.36
6f	**5b**	DMSO	7	94	4,580	8.37	63	32,000	1.97
6g	**5d**	DMSO	7	93	5,620	21.3	62	41,900	3.82

[a] Concentrations of **3** and A_2 were 0.32 M. [b] All reactions were performed with an oil bath temperature of 185 °C.

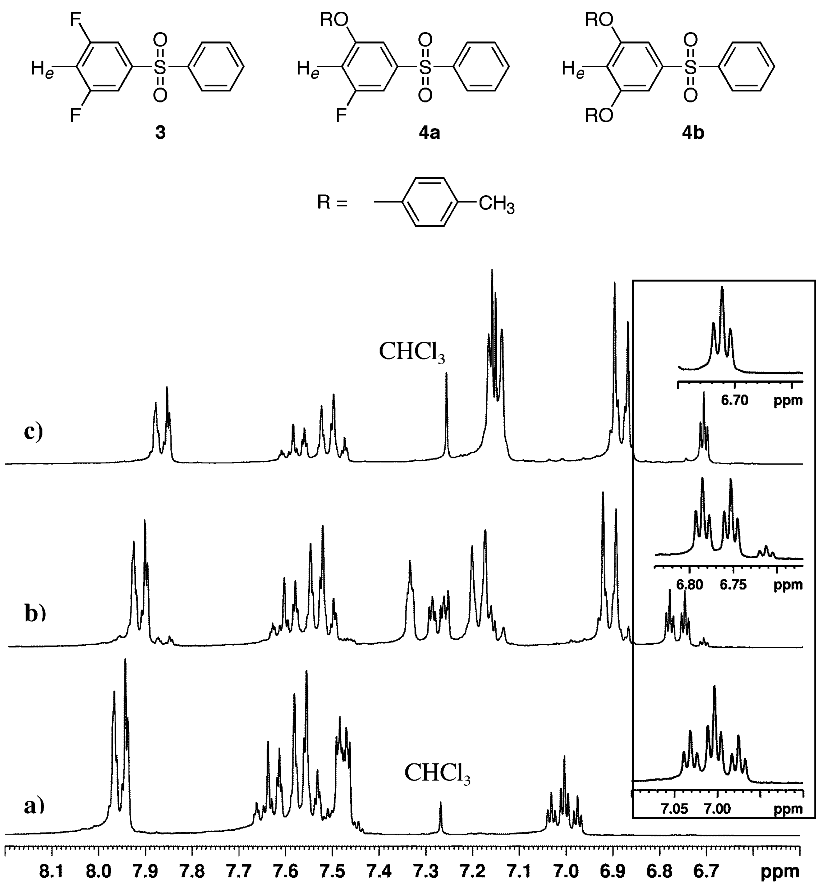


Figure 1. Aromatic region of the 300 MHz ^{1}H NMR spectra (CDCl$_3$) of (a) **3**, (b) **4a**, and (c) **4b**. The signals assigned to proton *e* in **3**, **4a**, and **4b** are highlighted in the box.

6e (95%). ^{1}H NMR (CDCl$_3$, δ): 6.78 (t, 1H); 6.99 (s, 4H); 7.26 (d, 2H); 7.58 (m, 3H); 7.86 (d, 2 H). ^{13}C NMR (CDCl$_3$, δ): 110.96, 112.02, 121.36, 127.81, 129.47, 133.59, 140.82, 144.53, 151.93, 159.59.

Results and Discussion

The synthesis of **3** was achieved as outlined in Scheme 1. A slight excess of 3,5-difluorophenylmagnesium bromide was reacted with benzenesulfonyl chloride in THF solution. After workup and recrystallization from ethanol/water followed by a recrystallization from hexanes, **3** was isolated as a yellow crystalline solid in 70% yield. The structure and purity of **3** were confirmed via ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy, GC/MS analysis, melting point (99−101 °C), and elemental analysis.

A number of authors have employed ^{13}C and ^{19}F NMR spectroscopy to probe the reactivity of electrophilic sites in aromatic halides.[14,17,26,27] 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.[26] Similar trends were observed with ^{19}F NMR chemical shifts. The ^{13}C and ^{19}F NMR chemical shift data for a variety of aryl difluoride monomers as well as that for **3** are listed in Table 1. A comparison of the data for **3** 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 **3** are sufficiently activated to undergo NAS reactions under relatively mild conditions. Presumably, the phenylsulfonyl group is activating the electrophilic sites through inductive effects rather than a direct resonance effect.

Model Reactions. The experimental reactivity and mechanism of fluoride displacement in **3** were probed via model reactions as outlined in Scheme 2. The phenoxide derivative of *p*-cresol was chosen as the nucleophile for the model reactions because its nucleophilic strength very closely mimics that of bisphenol A. Reaction of 1 equiv of *p*-cresol with **3** at 75 °C in NMP for 21 h afforded a product mixture consisting of ~7% of **3**, 86% of **4a**, and 7% of **4b** as determined by integration of the ^{1}H NMR spectrum. If the two electrophilic sites in **3** were of equal reactivity, a statistical product ratio of 25:50:25 (**3**:**4a**:**4b**) would have been observed. These results indicated a significant decrease in the reactivity of the electrophilic site in **4a** compared to those in **3**.

Further evidence for a decrease in reactivity on going from **3** to **4a** was gleaned from the reaction of 2 equiv of *p*-cresol with **3**, which required a temperature of 150 °C to reach completion and afford **4b** in the same 21 h reaction time. ^{13}C and ^{19}F NMR data (Table 1) also confirmed the decrease in reactivity on converting **3** to **4a**. For example the ^{19}F NMR chemical shift of **4a** was −107.70 ppm vs −106.32 ppm for **3**, indicating a significant increase in the electron density present at the electrophilic site in **4a**. Even though a significant decrease in the reactivity of **4a** was observed, the second displacement proceeded under relatively mild conditions to afford **4b** in quantitative yield (^{1}H NMR spectroscopy of a sample indicated complete conversion to **4b**), thus indicating sufficient reactivity to prepare high molecular weight PAEs.

Mechanistic Evidence. Confirmation that the model reactions proceeded via a typical S$_N$Ar mechanism, rather than a benzyne mechanism, is provided by ^{1}H and ^{13}C NMR spectroscopic analysis (Figures 1 and 2, respectively). In the ^{1}H NMR

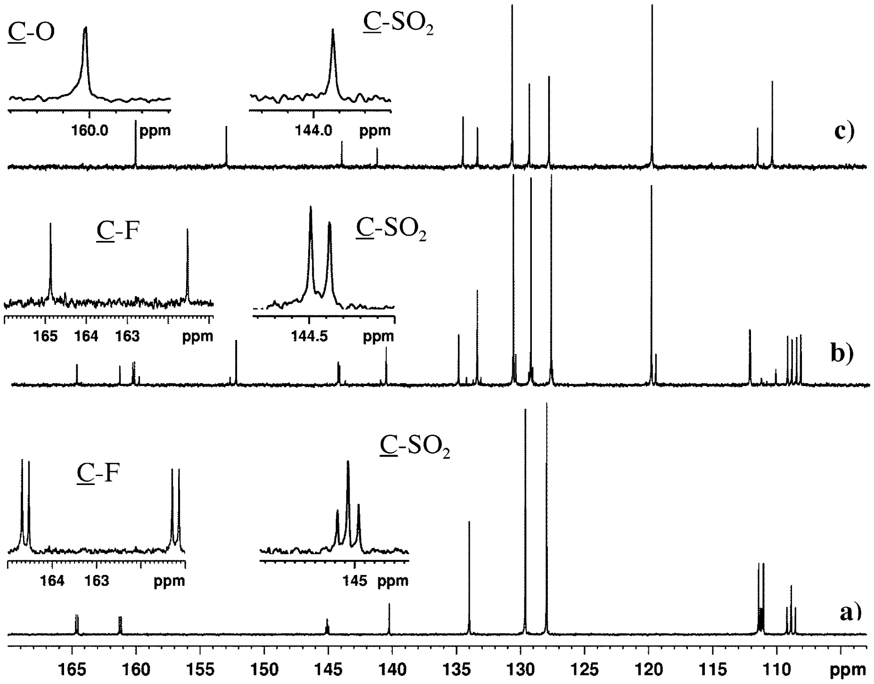
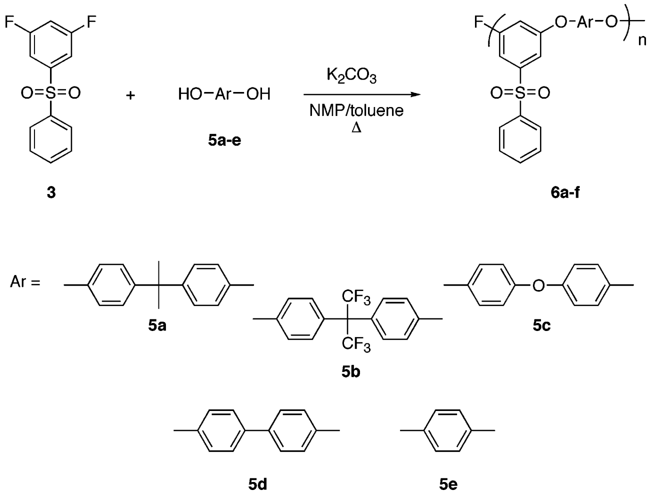


Figure 2. Aromatic regions of the 75.5 MHz ^{13}C NMR spectra (CDCl$_3$) of (a) **3**, (b) **4a**, and (c) **4b**.

Scheme 3



spectrum of **3**, 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 **4a** and **4b**, 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 **3**, **4a**, and **4b** (Figure 2).

Polymerization Reactions. Polymerization reactions of **3** with a variety of bisphenol monomers were carried out under typical NAS conditions as outlined in Scheme 3, and the molecular weight and polydispersity data are listed in Table 2. All of the polymerization reactions were accompanied by the formation of a significant percentage of oligomeric, potentially, cyclic species. Figure 3 displays a series of SEC traces for the reaction of **3** with **5b** in DMSO. Trace *a*, of the polymer precipitated from acidic water, displays a main polymer peak along with a relatively sharp signal for the oligomeric species. The oligomers were removed very efficiently via a reverse precipitation from THF/methanol as evidenced by traces *b* (after methanol precipitation) and *c* (subsequent precipitation from THF/methanol). Trace *d* is of the methanol soluble material, and it indicates the presence of at least two discrete species along with a continuum of lower molecular weight oligomeric species. Similar behavior was observed with all of the polymers prepared in this study. The relatively high percentage of cyclic material may be a result of the meta orientation of the electrophilic sites, the relatively low concentration of reagents, or both. Further experiments to gain a better understanding of these results are currently underway.

The number-average molecular weight values (relative to polystyrene standards), M_n, and percentage yields, for the materials precipitated from water and the reverse methanol precipitation, are listed in Table 2. The percentage yields upon precipitation from water were all greater than 90%. After the cyclic species were removed, the percentage yields dropped considerably with a low of 62% for the polymer prepared with **5d** in DMSO to a high of 70% for the polymer prepared with **5d** in NMP. The M_n values of samples from water precipitation were calculated including the low molecular species, resulting in extremely high PDI values being reported. However, after the cyclic and oligomeric species were removed, the M_n values increased significantly and a dramatic drop in the PDI values was observed. For example, the M_n value of **6b**, after the first precipitation from water, was only 5800 Da with a PDI of 10.9 while the sample after a reverse precipitation from methanol had a M_n value of 39 800 Da with a PDI value of 2.19.

The effects of polymerization solvent were explored by carrying out the same reactions in DMSO. From the M_n and PDI values of **6f** and **6g**, it appears that the effect of the more polar DMSO solvent was very limited with only a small decrease in the M_n values for the DMSO reactions when compared to the NMP reactions. The PDI values also decreased slightly for samples prepared in DMSO.

Because the polymerization reactions were performed at 185 °C, as opposed to the model reactions at 75 and 150 °C, it was important to determine whether the same S$_N$Ar mechanism was operating. Figure 4 displays the aromatic regions of the ^{1}H NMR spectra of **3**, **4b**, and **6b**. As was the case in the model reactions, the signal assigned to proton *e* in **3** appears as a triplet in **6b**,

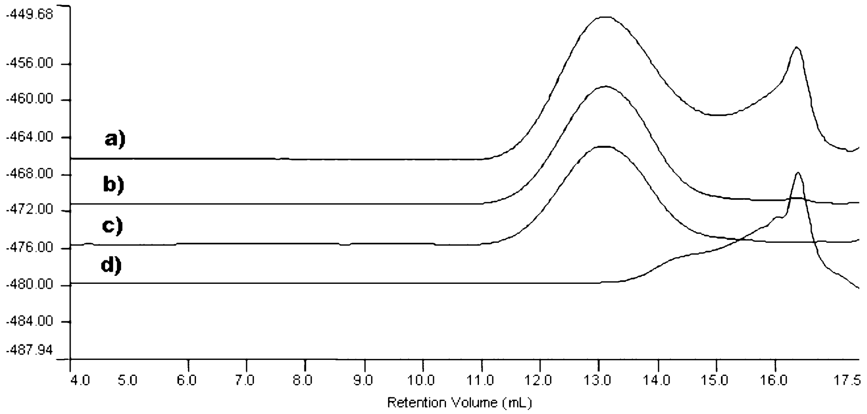


Figure 3. SEC traces of polymer sample **6f**: (a) reaction mixture precipitated from water, (b) sample from reverse THF/methanol precipitation, (c) final precipitation from THF/methanol, and (d) methanol soluble material.

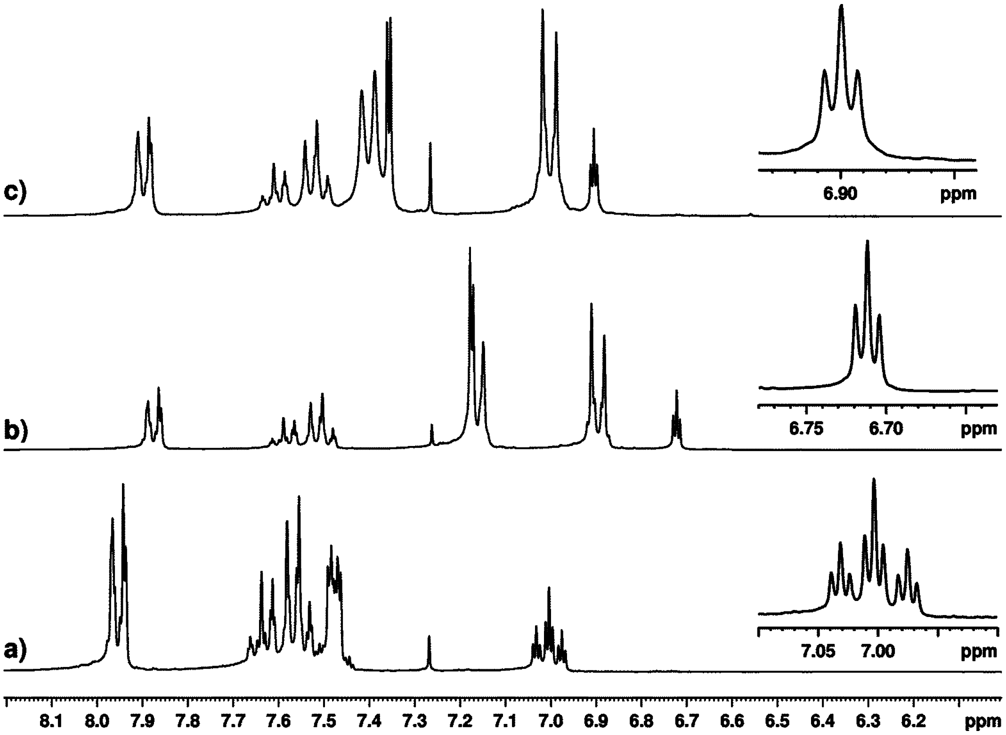


Figure 4. Aromatic region of the 300 MHz ^{1}H NMR spectra (CDCl$_3$) of (a) **3**, (b) **4b**, and (c) **6b**.

Table 3. Thermal Analysis Data for Poly(arylene ether)s Prepared from 3 and a Series of Bisphenol Monomers

polymer	T_g (°C)	$T_{d(10\%)}$ N$_2$ (°C)	$T_{d(10\%)}$ air (°C)
6a	142	530	507
6b	149	552	539
6c	136	569	539
6d	175	590	562
6e	148	554	539

thus confirming that no change in reaction mechanism occurred at the higher temperature. Further evidence for this conclusion was derived from analysis of the ^{13}C NMR spectrum of **6b,** which displayed only one signal for the carbon atoms in the new C−O bonds.

Thermal Analysis. The thermal properties of **6a**−**e** 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. The polymer prepared with **5c** displayed the lowest T_g value, 136 °C, while the more rigid **5d** afforded a PAE sample with a T_g of 175 °C.

The thermal stability of **6a**−**6e** was evaluated under nitrogen and air atmospheres. At a heating rate of 10 °C/min, under nitrogen, sample **6a**, the fluorinated sample **6b**, and the most aromatic sample, **6d**, possessed 10% weight loss temperatures of 530, 552, and 590 °C, respectively. In air, the corresponding values for **6a**, **6b**, and **6d** were 507, 539, and 562 °C, respectively.

Conclusions

A one-step synthesis of a B$_2$ monomer, **3**, for NAS synthesis of poly(arylene ether)s in which the activating group, phenyl sulfonyl, is located in the meta position has been carried out. The ^{19}F NMR chemical shift of the fluorine atoms in **3**, −106.32 ppm, indicated that the electrophilic sites were sufficiently activated to undergo a nucleophilic aromatic substitution reaction. Displacement of the first fluoride atom in **3**, with the phenoxide ion derived from *p*-cresol, was achieved in 21 h at 75 °C while displacement of the second fluoride atom required 150 °C to reach completion in the same time. 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 **4a**. Confirmation that the fluoride displacement reactions in **3** proceeded via an S_NAr mechanism was provided by ^{1}H and ^{13}C NMR data of model compounds and polymer samples. Amorphous poly(arylene ether)s, bearing a pendant phenylsulfonyl group, were prepared via the reaction of **3** with a variety of bisphenols under typical NAS conditions. Number-average molecular weights, after removal of oligomeric species, ranged from 11 220 Da, with hydroquinone, to 118 000 Da, with 4,4′-dihydroxydiphenyl ether. The poly(arylene ether)s possessed moderately high glass transition temperatures (T_g) which ranged from 136 to 175 °C but displayed excellent thermal stability with the 10% weight loss temperatures ranging from 507 and 530 °C, with bisphenol A, to 562 and 590 °C, with 4,4′-dihydroxybiphenyl, under air and nitrogen, respectively. Utilization of this methodology to prepare linear poly(arylene ether)s carrying a variety of pendant groups is currently being investigated.

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