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Utilization of *N*,*N*-diethyl-3,5-difluorobenzene sulfonamide to prepare functionalized poly(arylene ether)s

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ABSTRACT

A series of poly(arylene ether)s carrying a pendant diethyl sulfonamide group was prepared by the *meta* activated nucleophilic aromatic substitution reaction of a new aryl difluoride monomer, *N*,*N*-diethyl-3,5-difluorobenzene sulfonamide. The synthesis of *N*,*N*-diethyl-3,5-difluorobenzene sulfonamide was achieved via the one-step reaction of diethyl amine with commercially available 3,5-difluorobenzenesulfonyl chloride. Model reactions and NMR data indicated that the fluoride atoms were sufficiently activated by the sulfonamide group, located in the *meta* position, to provide access to high molecular weight poly(arylene ether)s. The corresponding poly(arylene ether)s, were prepared by reaction of *N*,*N*-diethyl-3,5-difluorobenzene sulfonamide with bisphenol A, bisphenol AF, 4,4′-biphenol, hydroquinone, resorcinol, and 4,4′-dihydroxydiphenyl ether. The polymers were characterized via NMR spectroscopy, size exclusion chromatography, thermogravimetric analysis, and differential scanning calorimetry. The sulfonamide based poly(arylene ether)s displayed moderate thermal stability with 5% weight loss temperatures ranging from 366 to 385 °C, but possessed relatively low glass transition temperatures, 72–142 °C.

1. Introduction

Poly(arylene ether)s, PAEs, are a class of engineering thermoplastics that possess excellent chemical and thermal resistance making them the material of choice for a wide variety of applications. PAEs are typically prepared via the nucleophilic aromatic substitution (NAS) polycondensation reaction of aryl difluorides or chlorides, which are activated toward NAS by the presence of a strong electron-withdrawing group located in the *ortho* or *para* position, with the *para* position being the more widely utilized, and bisphenolates prepared from the corresponding bis-phenols [1,2]. A number of activating groups have been employed such as the traditional sulfone [1–7], ketone [2,8–11], and phosphoryl groups [12–20], however, a wide variety of alternative activating groups have also been successfully employed including: azomethine [21], thianthrene [22], a number of heterocycles [23–32] and, more recently, the *N*,*N*-dimethylsulfonamide group [33].

1.1. Meta activated NAS reactions

In principle, a strong electron-withdrawing group, located in the *meta* position, should also provide sufficient activation to allow NAS reactions to proceed at reasonable rates. Indeed, the number of reports of *meta* activated NAS polycondensation reactions has increased in recent years. Our group has reported the synthesis of PAEs based on fluoro displacement of 3,5-difluorodiphenyl sulfone, **1** [34], 3,5-difluorobenzophenone, **2** [35], and 3,5-difluorotriphenylphosphine oxide, **3** [36]. In each case the activating group ends up as a pendant group rather than directly in the backbone and the polymers can be considered simply geometric isomers of the more common PAEs prepared from 4,4′-difluorodiphenyl sulfone, 4,4′-difluorobenzophenone, and 4,4′-difluorotriphenylphosphine oxide, respectively. Kim et al have also prepared biphenyl-based PAEs via the use of a *meta* trifluoromethyl group activated displacement of nitro groups [37–41]. A number of other examples of PAEs in which the activating group resides pendant to the backbone, have been reported, however, the orientation of the activating group was always *ortho* to the leaving group, typically fluoride [42–50].

1.2. Functional groups

The introduction of functional groups into PAEs provides the opportunity to tailor the chemical and physical properties to meet a specific need. Functional groups can either be introduced at the monomer stage (“pre”) or after the polymer has been prepared (“post”). Functional groups that are introduced “pre” must be able

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to withstand the rather rigorous conditions utilized in NAS reactions and not result in any side reactions. The introduction of functional groups, via a "post" procedure, must not disturb the polymer backbone or lead to any crosslinking. The ideal functional group would be one that could be carried into the polymer and be subsequently converted to a variety of additional moieties.

In this report we will describe our efforts to prepare PAEs that carry a pendant sulfonamide moiety, located in the *meta* position relative to the ether bonds. Thus, the synthesis, characterization, and polymerization behavior of *N*,*N*-diethyl-3,5-difluorobenzene sulfonamide, **4**, will be described. Since the sulfonamide group in the 3,5-difluorobenzene sulfonamide is located in the *meta* position, relative to both fluorine atoms, it is anticipated that a wide variety of *N*-substitutions, with potentially bulky groups, could provide a useful method to introduce a multitude of functional groups to the resulting PAEs. For example, a *N*,*N*-diaryl-3,5-difluorobenzene sulfonamides could be utilized to introduce aryl bromide or iodide moieties. Alternatively, *N*-propargyl sulfonamide structures would provide access to "clickable" systems.

2. Experimental

2.1. Materials

Powdered K_2CO_3 (Sigma Aldrich) was dried at 130 °C in an oven before use. 3,5-Difluorobenzene sulfonyl chloride was purchased from Oakwood Products and was used as received. Bisphenol A (Sigma Aldrich), 4,4′-biphenol (Sigma Aldrich), 4,4′-dihydroxydiphenyl ether (Sigma Aldrich), DPE, Resorcinol (Sigma Aldrich) and Bisphenol AF (TCI America) were recrystallized from toluene, followed by drying under vacuum prior to use. Hydroquinone (Sigma Aldrich) was recrystallized from methanol/water, followed by drying under vacuum prior to use. *N*-methylpyrrolidone (Sigma Aldrich), NMP, was dried over and distilled from calcium hydride under a nitrogen atmosphere prior to use. 4-*tert*-Butylphenol (Sigma Aldrich) and diethyl amine (Sigma Aldrich) were used as received.

2.2. Instrumentation

^1H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were acquired 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 an appropriate deuterated solvent (DMSO-d_6 or $CDCl_3$) at a concentration of (~30 mg/0.7 mL). GC/MS analyses were performed using a Hewlett–Packard (HP) 6890 Series GC and a HP 5973 Mass Selective Detector/Quadrupole system. DSC and TGA were carried out on TA Instruments DSC Q200 (under nitrogen) and TGA Q500 (under nitrogen or air), respectively, at a heating rate of 10 °C/ min. Size Exclusion Chromatography (SEC) analysis was performed using a system consisting of a Viscotek Model 270 Dual Detector (viscometer and light scattering) and a Viscotek Model VE3580 refractive index detector. Two Polymer Laboratories 5 μm PL gel Mixed C columns (heated to 35 °C) were used with tetrahydrofuran as the eluent and a Thermoseparation Model P1000 pump operating at 1.0 mL/min. Number average molecular weights, *Mn*, were determined with the light scattering and refractive index (RI) detectors and the dispersity was determined using the RI signal (calibrated with polystyrene standards). Melting points were determined on a MEL-TEMP apparatus and are uncorrected. Elemental analyses were obtained from Midwest Microlabs, Inc., Indianapolis, IN. Matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF-TOF) was performed at the Mass Spectrometry & Proteomics Facility at The Ohio State University, Columbus, OH, on a Bruker Daltonics ultrafleXtreme™ (Bruker Daltonics, Breman, Germany) mass spectrometer operated in reflectron, positive ion mode with a N_2 smartbeam II™ laser. Laser power was used at the threshold level required to generate signal and acquired at 1000 Hz until suitable data was obtained. The instrument was calibrated with the Peptide Calibration Standard II purchased from Bruker Daltonics which contains Angiotensin II, Angiotensin I, Substance P, Bombesin, ACTH clip 1-17, ACTH clip 18-39, Somatostatin 28, Bradykinin Fragment 1–7, Renin Substrate Tetradecapeptide porcine with a covered mass range: ~700 Da to 3200 Da. Samples were prepared in THF to approximately 50 pmol/μL. 2,5-Dihydroxybenzoic acid (DHB) was used as the matrix prepared as a saturated solution in THF. Allotments of 5 μL of matrix and 1 μL of sample were thoroughly mixed together; 0.5 mL of this was spotted on the target plate and allowed to dry.

2.2.1. Synthesis of (*N*,*N*-diethyl)-3,5-difluoro-benzenesulfonamide (**4**)

To a 250 mL Erlenmeyer flask were added 3,5-difluorobenzenesulfonyl chloride (5.00 g, 23.5 mmol) and 50 mL of dichloromethane. A 26% solution of diethylamine (5.0 mL, 52.7 mmol) in water was added to the flask followed by DI water (40.0 mL). The solution was heated to 40 °C for 24 h with vigorous stirring. The reaction mixture was then extracted twice with 25 mL portions of dichloromethane and the organic layer was subsequently washed with 50.0 mL of 5% HCl solution, DI water, 50.0 mL of 0.1 M NaOH solution, and finally water. The organic layer was then evaporated under reduced pressure to yield a yellow solid, which was then recrystallized from hexanes to afford 3.5 g (61%) of the title compound as a light yellow crystalline solid (m.p. 50–51 °C). ^1H NMR ($CDCl_3$, δ): 7.4–7.5 (m, 2 H), 7.00 (tt, 1 H), 3.2-3.3 (q, 4 H), 1.2–1.3 (t, 6 H); ^{13}C NMR ($CDCl_3$, δ): 14 (s), 42 (s), 107 (t), 110 (dd), 143 (t), 162.9 (dd) all with respect to TMS at 0.0 ppm; ^{19}F NMR (DMSO-d_6, δ): −106.3. GC/MS: *m*/*z*: 249. Elemental analysis: Calc. Anal. for $C_{10}H_{13}F_2NSO_2$: C, 48.16; H, 5.26; Found: C, 48.07; H, 5.13.

2.2.2. Model reaction of (**4**)

To a 25 mL round-bottomed flask were added **4** (0.300 g, 1.2 mmol), K_2CO_3 (0.497 g, 3.6 mmol), *t*-butylphenol (0.360 g, 2.4 mmol) and NMP (1.875 mL). The resulting mixture was heated to 185 °C for 21 h with stirring and was monitored by removing aliquots for GC/MS analysis, which indicated nearly quantitative displacement of the fluorides. The solution was then diluted to 100 mL in $CHCl_3$ and extracted 3 times with both 10% HCl solution and saturated $NaHCO_3$. The solution was then stirred in water overnight, dried over $MgSO_4$ and dried under vacuum to yield 0.352 g (60%) of an off-white solid, **5**. ^1H NMR ($CDCl_3$, δ): 1.02 (t, 6 H), 1.25 (s, 18 H), 3.12 (q, 4H), 6.70 (t, 1H), 6.88 (d, 4 H), 6.99 (d, 2 H), 7.29 (d, 4 H); ^{13}C NMR ($CDCl_3$, δ): 14.1, 31.5, 34.4, 42.0, 110.3, 111.3, 119.1, 126.9, 142.9, 147.5, 153.2, 159.6.

2.2.3. General procedure for polymerization reactions (**7a**–**f**)

A typical polymerization reaction will be described using Bisphenol A, **6a**. To a 25 mL round-bottomed flask, equipped with a stir bar, reflux condenser, and gas inlet, was added **4** (0.500 g, 2.0 mmol), K_2CO_3 (0.832 g, 6.30 mmol), **6a** (0.472 g, 2.07 mmol) and NMP (3.0 mL). The reaction mixture was heated to 185 °C for 21 h at which point it was cooled to ~100 °C and slowly poured into water (400 mL) with vigorous stirring. The solution was allowed to stir for another 30 min before filtering and drying the resulting solid under vacuum. The polymer was dissolved in a minimum amount of THF and then re-precipitated in ethanol/water (400 mL:40 mL) containing a few drops of concentrated HCl. The resulting white precipitate, 0.66 g (68%) was isolated via

filtration and dried under vacuum prior to analysis. ^{1}H NMR ($CDCl_3$, δ): 1.08 (t, 6 H), 1.68 (b, 6 H), 3.18 (q, 4 H), 6.82 (t, 1 H), 6.93 (d, 4 H), 7.06 (d, 2 H), 7.22 (d, 4 H). ^{13}C NMR ($CDCl_3$, δ): 14.1, 31.0, 42.1, 42.4, 110.6, 111.8, 119.1, 128.4, 143.0, 146.8, 153.6, 159.4.

Polymerization reactions with the remaining bis-phenols were carried out in a similar fashion.

7b (64%): ^{1}H NMR ($CDCl_3$, δ): 1.11 (t, 6 H), 3.22 (q, 4 H), 6.94 (t, 1H), 7.02 (d, 4 H), 7.21 (d, 2H), 7.41 (d, 4 H); ^{13}C NMR ($CDCl_3$, δ): 13.1, 42.1, 112.6, 113.6, 118.7, 120.6 (q, CF_3), 129.6, 132.1, 143.9, 156.6, 158.2.

7c (64%): ^{1}H NMR ($CDCl_3$, δ): 1.12 (t, 6 H), 3.22 (q, 4 H), 6.91 (t, 3 H), 7.12 (d, 4 H), 7.15 (d, 2 H), 7.56 (d, 4 H); ^{13}C NMR ($CDCl_3$, δ): 14.3, 42.2, 111.0, 112.2, 128.8, 136.9, 143.4, 155.3, 159.4.

7d (70%): ^{1}H NMR ($CDCl_3$, δ): 1.11 (t, 6 H), 3.21 (q, 4 H), 6.78 (t, 1 H), 7.04 (b, 8 H), 7.06 (d, 2 H); ^{13}C NMR ($CDCl_3$, δ): 14.2, 42.1, 110.0, 110.8, 120.3, 121.3, 143.2, 151.0, 154.0, 159.8.

7e (41%): ^{1}H NMR ($CDCl_3$, δ): 1.11 (t, 6 H), 3.22 (q, 4 H), 6.84 (t, 3 H), 7.06 (s, 4 H), 7.10 (d, 2 H); ^{13}C NMR ($CDCl_3$, δ): 14.1, 42.1, 110.6, 111.5, 121.3, 143.5, 152.2, 159.4.

7f (38%): ^{1}H NMR ($CDCl_3$, δ): 1.03 (t, 6 H), 3.14 (q, 4 H), 6.67 (t, 3 H), 6.73 (dd, 2 H), 6.78 (t, 1 H), 7.29 (t, 1H); ^{13}C NMR ($CDCl_3$, δ): 14.1, 42.1, 110.7, 111.8, 112.7, 114.9, 131.2, 143.6, 157.3, 158.5.

3. Results and discussion

3.1. Monomer synthesis and characterization

The synthesis of *N*,*N*-diethyl-3,5-difluorobenzene sulfonamide, **4**, was achieved via the one-step procedure outlined in Scheme 1. Reaction of commercially available 3,5-difluorobenzenesulfonyl chloride with an excess of diethylamine afforded the desired compound in 61% yield after recrystallization twice from hexanes. Confirmation of the structure of **4** was provided by a combination of ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy, gas chromatography/mass spectrometry (GC/MS), and elemental analysis. The ^{13}C NMR spectrum of **4** is presented in Fig. 1.

Due to spin–spin coupling with the two fluorine atoms present on the ring, carbon atoms **a**–**d** all experience some degree of splitting and the coupling constants vary with their position relative to the C–F bonds. Carbon **a** gives rise to a triplet at 107 ppm, the resonance for carbon **c** is a doublet of doublets centered at 110 ppm, carbon **d**, at 143 ppm, appears as a triplet, and carbon **b** gives rise to a doublet of doublets at 162.9 ppm. The signals for carbon atoms **e** and **f** were identified as singlets and were found at 42 and 14 ppm, respectively.

The reactivity of the electrophilic sites in **4**, toward NAS reactions, was probed via a combination of ^{13}C and ^{19}F NMR spectroscopy as well as model reactions (Scheme 1). A number of authors have utilized NMR spectroscopy as a guide for determining the ability of fluoride atoms to be displaced by nucleophiles. [33,51,52] In general, more reactive species exhibit both ^{13}C and ^{19}F NMR chemical shifts that are considerably more downfield than those from less reactive species. For example, the ^{19}F NMR chemical shifts of 4,4′-difluorodiphenyl sulfone and 4,4′-difluorobenzophenone are reported as −104.1 and −106.1 ppm, respectively. Fluorobenzene, which is considered to be unreactive in NAS reactions, has a ^{19}F NMR chemical shift of −112 ppm.

The ^{19}F NMR chemical shift for the fluorine atoms in compound **4** was found to be −106.3 ppm. For comparison purposes, the ^{19}F NMR chemical shifts for the fluorine atoms in *N*,*N*-dimethyl-2,4-difluorobenzene sulfonamide, which was also successfully converted to a PAE, were −103.08 (*para*) and −104.82 (*ortho*) ppm, respective to the sulfonamide group [33]. The fluorine data indicate that the fluorine atoms in **4** were considerably less reactive than those located in the *ortho* and *para* positions, however, given that the ^{19}F NMR chemical shift of the fluorine atoms in **4** is similar to that of 4,4′-difluorobenzophenone (−106.1 ppm) they should still be readily displaceable by phenoxide nucleophiles. The relative ease of displacement of the fluorine atoms in **4** was confirmed experimentally by carrying out a model reaction, using 4-*t*-butylphenoxide as the nucleophile, as outlined in Scheme 1. Displacement of both fluorine atoms, as confirmed by GC/MS analysis, was completed after 21 h at 185 °C, which indicated a high potential for the successful preparation of the corresponding poly(arylene ether)s.

3.2. Polymer synthesis

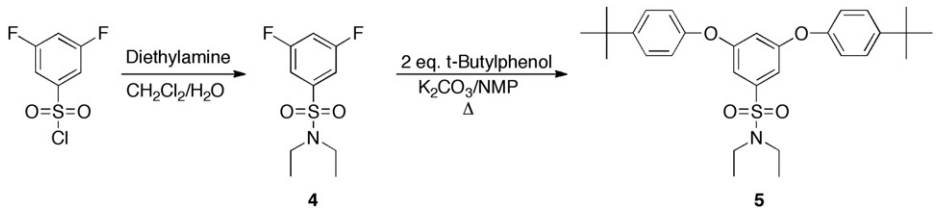
As outlined in Scheme 2 a series of PAEs was prepared from **4** and a variety of bis-phenols in *N*-methylpyrrolidinone (NMP) with potassium carbonate utilized to prepare the corresponding bisphenolate *in situ*. In order to be consistent, all of the reactions were carried out at 185 °C for 21 h, followed by precipitating the reaction mixture into a large excess of water to afford the corresponding polymer as an off-white solid. The polymer was isolated via filtration and dried prior to being analyzed by Size Exclusion Chromatography (SEC), ^{1}H and ^{13}C NMR spectroscopy, Thermogravimetric Analysis (TGA), and Differential Scanning Calorimetry (DSC).

The ^{13}C NMR spectrum of polymer **7a** is presented in Fig. 2 and indicates that **4** was successfully converted to the desired polymer. The triplets, representing carbon atoms *a* and *d*, and doublets of doublets, arising from carbon atoms *b* and *c*, resulting from fluorine coupling in **4**, have been reduced to singlets after conversion to the corresponding aryl ether system.

In addition, the signals arising from the carbon atoms, labeled *g*–*l*, in the Bisphenol-A component are now present.

3.3. Cyclic oligomer formation

In previous polycondensation reactions with 3,5-difluoro aromatic systems it was observed that the formation of linear polymer was always accompanied by the formation of cyclic oligomeric species and the current monomer showed similar behavior. Fig. 3 displays the SEC traces of the crude polymer **7a**, the polymer after reprecipitation from ethanol/water (90:10) and the ethanol/water soluble material. In the trace of the crude material there is evidence of some discrete sized oligomeric material in the lower molecular weight region while, after the reprecipitation process, their presence was much less apparent. The trace of the ethanol/



4 5

Scheme 1. Synthetic procedure for the synthesis of **4** and subsequent model reaction for determination of the reactivity of its electrophilic sites.

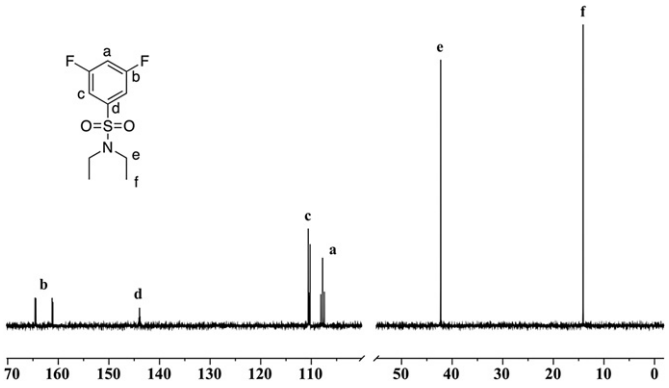


Fig. 1. 75.5 MHz ^{13}C ($CDCl_3$) NMR spectrum of monomer **4**.

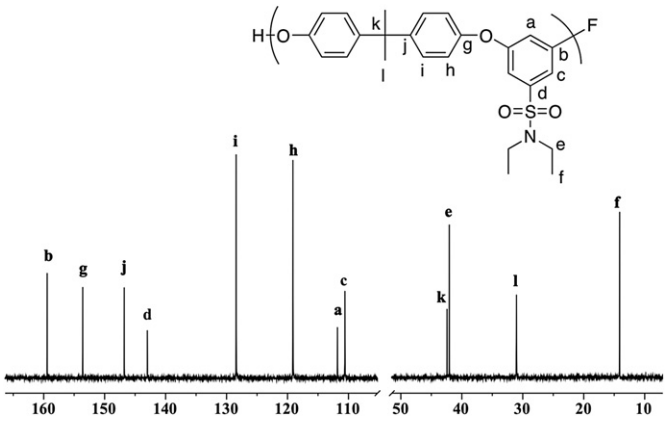


Fig. 2. 75.5 MHz ^{13}C ($CDCl_3$) NMR spectrum of polymer **7a**.

water soluble fraction indicated that at least two discernable species along with some of the lower molecular weight, presumably linear, material had been removed.

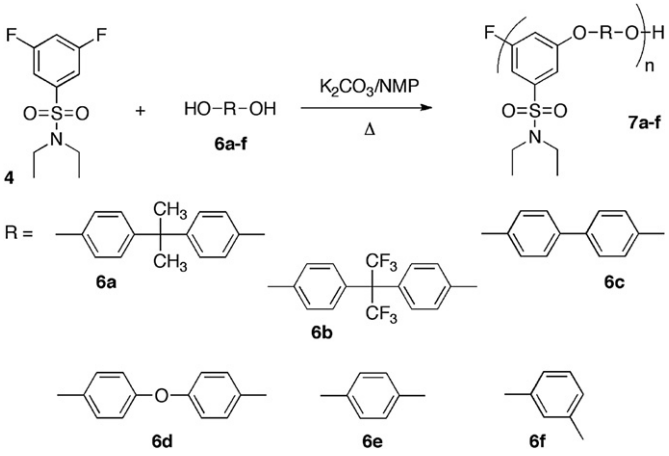
The ethanol/water soluble material was further analyzed via mass spectrometry and the spectrum is shown in Fig. 4. The spectrum clearly shows the presence of cyclic species with the dimer ($m/z = 913.327$, $n = 2 + K^+$), trimer ($m/z = 1350.434$, $n = 3 + K^+$), and tetramer ($m/z = 1787.566$, $n = 4 + K^+$) predominating, although some higher molecular weight cyclic species are also present. All of the signals corresponded to the mass of a discrete cyclic species plus a potassium ion. The regular spacing between the signals corresponds exactly to the repeat unit formula weight of one Bisphenol A and one monomer **4**.

3.4. Molecular weight determination

The number average molecular weights, M_n, of polymers **7a**–**f** were determined via SEC using the light scattering and refractive index detectors and the data is summarized in Table 1. The samples were evaluated after removing the low molecular weight cyclic species. All of the polymers, with the exception of the resorcinol-based material, **7f**, possessed M_n values above 20,000 Daltons (Da). The Bisphenol-AF material (**7b**) had a M_n value of 85,500 Da and the hydroquinone polymer (**7e**) had a M_n of 20,400 Da, which correspond to 157 and 64 repeat units, respectively. The dispersity values for **7a**–**7f**, determined using a conventional calibration on the refractive index detector, ranged from a low of 1.9 (**7a**) to a high of 3.2 (**7c**). The much lower *M*n value (6300 Da) observed for the resorcinol system (**7f**), may result from the *meta* orientation of the reactive groups found in both **4** and resorcinol, leading to a higher percentage of cyclic species, as well as the lower reactivity of the phenoxide groups. Despite the reasonably high M_n values of polymers **7a**–**7f**, they were found to be soluble in a wide variety of solvents including chloroform, tetrahydrofuran (THF), and *N*-methylpyrolidinone (NMP), but were insoluble in water and alcohols.

3.5. Thermal properties

The thermal properties of polymers **7a**–**f** were evaluated by a combination of Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry. The TGA thermograms for polymers **7a** and **7b**, under nitrogen, are shown in Fig. 5. Under a nitrogen atmosphere all of the polymers exhibited a two-stage decomposition profile with the first stage being attributed to the loss of the diethyl sulfonamide group. In fact, the percentage weight loss for the first step very closely approximated the percentage, by weight, of the diethyl sulfonamide group relative to the repeat unit of the polymer. For example, the calculated weight percentages of diethyl sulfonamide in the Bis-A (**7a**) and Bis-AF (**7b**) polymers were 31.1 and 25.0%, respectively, while the experimental% losses, under



Scheme 2. Reaction scheme for polycondensation reactions of monomer **4** with a variety of bis-phenols.

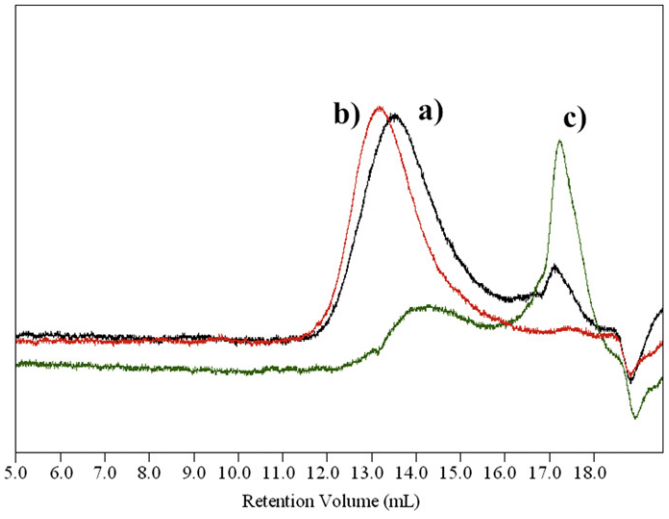


Fig. 3. SEC traces of polymer **7a**: (a) crude, (b) reprecipitated from ethanol/water (90:10), and (c) the ethanol/water soluble material.

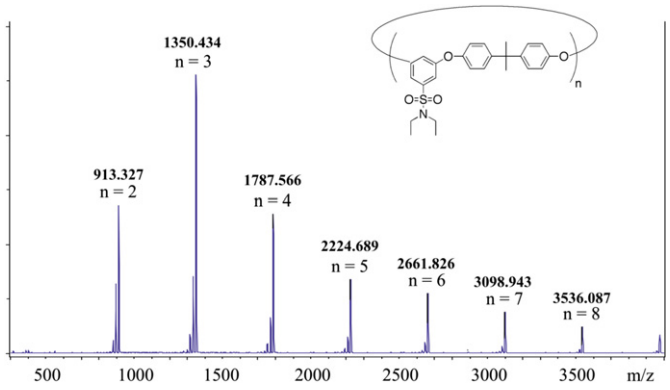


Fig. 4. MALDI-TOF MS spectrum of the ethanol/water soluble material from the reaction utilized to prepare **7a**. The repeat unit formula weight was calculated as 437.18 g/mol.

Table 1
Reaction conditions, percentage yield, molecular weight, dispersity, and thermal analysis data for polymers prepared from monomer **4** and various bis-phenols.

Polymer	Bisphenol	% yield	Mn[a] (Da)	Dispersity	T_g[b] (°)	$T_{d\ (5\%)}$[c] N_2 (°C)	$T_{d\ (5\%)}$[c] air (°)
7a	**6a**	66	27,900	1.9	117	388	381
7b	**6b**	64	85,500	2.2	136	395	385
7c	**6c**	64	30,300	3.2	142	400	388
7d	**6d**	70	39,600	2.2	102	396	366
7e	**6e**	48	20,500	2.3	102	381	381
7f	**6f**	38	6300	1.9	72	382	382

[a] Determined via SEC analysis.
[b] Heating rate of 10 °C/min.
[c] Heating rate of 10 °C/min.

nitrogen, during the first step of degradation were 27.0 and 22.9%. Similar results were observed under air atmospheres and the weight percent data for all of the polymers is summarized in Table 2.

The DSC traces (Fig. 6) for **7a**–**f** indicated that completely amorphous polymers had been prepared with only glass transition temperatures, T_g, being observed in heating traces up to 300 °C. The highest T_g value was 142 °C for the more rigid, biphenyl-based polymer (**7c**) while the lowest was only 72 °C for the resorcinol-based polymer (**7f**). However, the very low T_g value (72 °C) observed for **7f** might be attributed, in part, to its low molecular weight, 6300 g/mol. For comparison purposes the T_g values of the biphenyl-based PAE materials prepared from 3,5-difluorodiphenyl sulfone, **1**, 3,5-

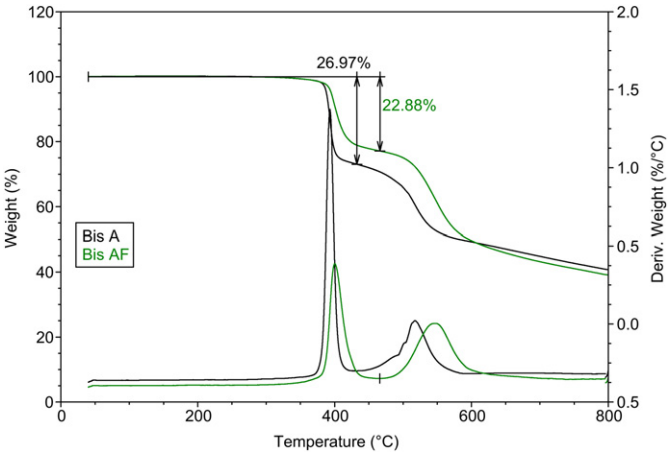


Fig. 5. Thermogravimetic analysis data, weight percentage and first derivative of weight percent, for polymers **7a** and **7b**, under nitrogen.

Table 2
Calculated and experimental values for the percentage weight loss of the diethyl sulfonamide group in polymers **7a**–**f**. The experimental data was determined from the 1st derivative plots of weight percent versus temperature curves.

Polymer	Weight% SO_2NEt_2	1st Step% loss (N_2)	1st Step% loss (air)
7a	31.1	27.0	29.2
7b	25.0	22.9	25.2
7c	34.3	29.1	29.7
7d	33.9	31.6	40.4
7e	42.6	41.3	43.5
7f	42.6	42.8	41.1

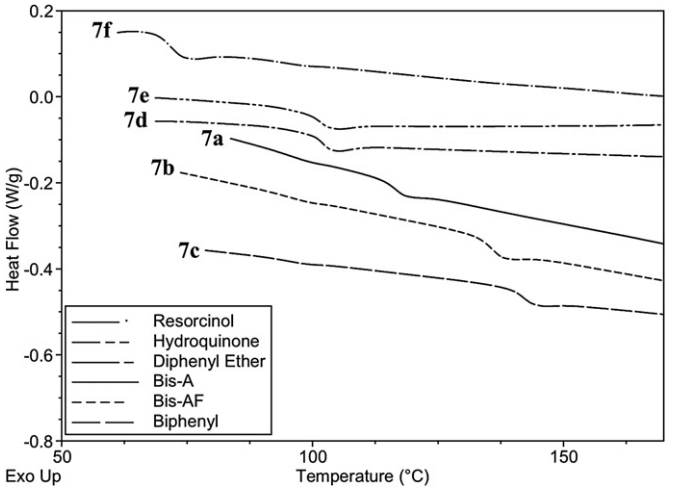


Fig. 6. Differential scanning calorimetry traces of polymers **7a**–**f**, under a nitrogen atmosphere at a heating rate of 10 °C/min.

difluorobenzophenone, **2**, and 3,5-difluorotriphenylphosphine oxide, **3**, were 175, 126, and 175 °C, respectively.

The backbones of the diphenyl ether and hydroquinone systems, **7d** and **7e**, can be considered as geometric isomers of poly(1,4-phenylene oxide), which has a T_g of 95 °C. The T_g values of **7d** and **7e** were both found to be 102 °C, only slightly higher than that of poly(1,4-phenylene oxide). The presence of the diethylsulfonamide group most likely increases the free volume in the systems, which should lead to a lower T_g. However, it appears that the free volume effects are offset by the strong intermolecular forces resulting from the polarity of the sulfonamide group, which hinder backbone rotation, leading to a T_g value similar to that of the relatively flexible poly(1,4-phenylene oxide).

4. Conclusions

The synthesis and application of *N*,*N*-diethyl-3,5-difluorobenzene sulfonamide, **4**, has been evaluated as a route to synthesize poly(arylene ether)s with pendant sulfonamide groups. The synthesis of **4** was achieved in relatively high yield via a straightforward one-step process using commercially available reagents. While the electrophilic sites in **4** were shown to be considerably less reactive than those activated by a sulfonamide located in the *ortho* and *para* positions, they were sufficiently reactive to prepare high molecular weight poly(arylene ether)s. The reaction of **4** with a variety of bis-phenols, under typical NAS conditions, afforded completely amorphous poly(arylene ether)s bearing a pendant diethylsulfonamide group located *meta* to the newly formed ether bonds. Number average molecular weights as high as 85,500 Da were achieved. The poly(arylene ether)s

possessed relatively low glass transition temperatures (T_g) which ranged from 72 to 142 °C, but displayed relatively good thermal stability with the 5% weight loss temperatures ranging from 381 to 400 °C in nitrogen. The thermal decomposition of the polymers followed a two-step pathway in which the first step was assigned to the loss of the sulfonamide group, followed by backbone degradation. Further work involving the introduction of more sterically demanding substituents on the sulfonamide moiety is ongoing.

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