Macromolecules

ARTICLE

pubs.acs.org/Macromolecules

Sulfonamide as an Activating Group for the Synthesis of Poly(aryl ether sulfonamide)s by Nucleophilic Aromatic Substitution

Nathaniel T. Rebeck and Daniel M. Knauss*

Renewable Energy Materials Research Science and Engineering Center, Department of Chemistry and Geochemistry, Colorado School of Mines, Golden, Colorado 80401, United States

ABSTRACT: Poly(aryl ether sulfonamide)s were produced utilizing the sulfonamide moiety as a new activating group for nucleophlic aromatic substitution polymerization. The activated monomer, 2,4-difluoro-*N*,*N*-dimethylbenzenesulfonamide, was synthesized in high yields through a simple substitution reaction between 2,4-difluorobenzenesulfonyl chloride and dimethyl amine. The reactivity of this monomer in a nucleophilic aromatic substitution mechanism was estimated using semiempirical calculations at the PM3 level, as well as by ^{1}H, ^{13}C and ^{19}F NMR spectroscopy. The data support the sulfonamide as sufficiently electron-withdrawing to activate aryl fluorides for substitution by phenoxide nucleophiles. Model reactions with *tert*-butylphenol confirm that the aryl fluorides of 2,4-difluoro-*N*,*N*-dimethylbenzenesulfonamide can be displaced in quantitative yields and suggest the process is suitable for forming polymers. A variety of novel polymers were produced employing bisphenol A, 4,4′-biphenol, bisphenol AF and hydroquinone as comonomers. The polymers were characterized by gel permeation chromatography, solution viscometry, NMR spectroscopy, thermogravimetric analysis, and differential scanning calorimetry. The high molecular weight poly(aryl ether sulfonamide)s exhibit moderate to high glass transition temperatures ranging from 163 to 199 °C. The polymers were shown to be thermally stable with 5% weight loss occurring from 398 to 442 °C in a nitrogen atmosphere.

INTRODUCTION

Poly(aryl ether)s have continued to be researched as an important class of polymers due to their excellent thermal stability, good mechanical properties, and ease of functionalization. The majority of poly(aryl ether)s are synthesized by reacting an activated diaryl halide and a bisphenol through a nucleophilic aromatic substitution (S_NAr) mechanism. S_NAr provides a flexible, inexpensive route to these high performance materials and can be accomplished when an electron-withdrawing group activates an aryl halide or aryl nitro for substitution by a nucleophile. The reaction occurs through a two-step mechanism in which the nucleophile first attacks and forms the tetrahedral intermediate Meisenheimer complex, and then upon loss of the halide leaving group, aromaticity is regained and the product ether is formed. The electron-withdrawing group promotes this reaction in two ways. First, the electron-withdrawing nature of the activating group removes electron density from the carbon *ipso* to the fluorine, increasing the rate of attack by the nucleophile.[1,2] Second, the electron-accepting character of the activating group lowers the activation energy by stabilizing the Meisenheimer complex.[3,4] A variety of groups have been used to activate aryl fluorides for substitution by phenoxide nucleophiles and to provide an assortment of characteristics to the polymer. The most commonly used and most highly activating groups for polymerization have been sulfones[4,5] and ketones,[4,6] but many other groups have also been shown to be activating for polymerization, including amides,[7,8] azomethine,[9] sulfide,[10] thianthrene,[11,12] and phosphine oxides.[13−15]

Activating groups are typically positioned to activate the *ortho* and *para* positions for nucleophilic substitution, although some examples of *meta* substitution have been demonstrated for strong activating groups.[16,17] Substitution at the *ortho* position, while supported by resonance, is found to be slower due to steric hindrance.[18,19] The difference in reactivity has even been exploited to produce exclusively *para* substitution in some monomers.[18] Most poly(aryl ether)s are formed with 1,4-aryl linkages, forming polymers with rigid linear backbones. Polymers with kinked backbones, formed by reaction at *ortho*-substituted aryl halides, have been less well investigated; however, a few examples exist. Poly(aryl ether)s with pendent sulfones and ketones have been synthesized from sulfone and ketone activated 2,4 and 2,6-difluoroaromatics and a variety of bisphenols.[20] Poly(pyridine ether)s have also been synthesized in the bulk through the substitution of 2,6-difluoropyridine by various silylated bisphenols.[21] Multiple research groups have produced aromatic polyethers with pendent nitriles from 2,4 and 2,6-dinitro or dihalobenzonitriles using the more strongly activating nitrile group.[22−27] These studies show that pendent activating groups must be strongly activating to overcome the decreased reactivity from the steric crowding at the *ortho* position.

The sulfonamide moiety has also been shown to be a stable group that can stand up to an array of reaction conditions and has led to the extensive use of sulfonamides as protecting groups for amines[28−30] and sulfonic acids[31] during multistep syntheses. Sulfonamides have also been shown to activate aryl halides at the *para* position for nucleophilic displacement reactions under very mild conditions.[32−36] The mild reaction conditions suggest that the sulfonamide is strongly activated. Surprisingly, to the best of

Received: May 19, 2011
Revised: July 13, 2011
Published: August 11, 2011

our knowledge, sulfonamides have never been used to activate for S_NAr polymerization.

Sulfonamides allow for the incorporation of a new functional group into poly(aryl ether)s leading to a variety of new polymers. Sulfonamide activation of fluorines at both the *ortho* and *para* positions of a ring for substitution can produce polymers with pendent sulfonamides, making available a latent functionality that could be converted into a sulfonic acid. The work presented here shows the utility of the sulfonamide moiety in producing new functional poly(aryl ether)s.

EXPERIMENTAL SECTION

Materials. 2,4-Difluorobenzenesulfonyl chloride (Sigma-Aldrich, 97%), dimethylamine (Eastman Kodak, 26% solution in water), and dimethylformamide (Mallinckrodt Chemical, ChromAR) were used as received. 4-*tert*-Butylphenol (Sigma-Aldrich, 99%) was recrystallized from petroleum ether. 4,4′-Isopropylidenediphenol (Bisphenol A) (Sigma-Aldrich, 97%) and 4,4′-(hexafluoroisopropylidene)diphenol (Bisphenol AF) (Sigma-Aldrich, ≥98%) were twice recrystallized from toluene. Bisphenol AF was further purified by sublimation under reduced pressure. 4,4′-Biphenol (Sigma-Aldrich, 97%) was twice recrystallized from acetone then sublimed under reduced pressure. Hydroquinone (Fisher Chemical, purified) was recrystallized from acetone. Potassium carbonate (Fisher Chemical) was dried overnight under vacuum. *N*-Methylpyrrolidinone (NMP) (Mallinckrodt Chemical, ChromAR) was twice distilled from phosphorus pentoxide under reduced pressure. 1,3-Dimethyl-3,4,5,6-tetrahydro-2-(1*H*)-pyrimidinone (DMPU) (Sigma-Aldrich, 98%) was distilled from calcium hydride under reduced pressure.

Characterization. Thermogravimetric analysis (TGA) was performed on a Seiko TGA/DTA320 at a heating rate of 10 °C/min under a nitrogen atmosphere. The glass transition temperatures (T_g's) were measured on a Perkin-Elmer Pyris 1 differential scanning calorimeter running Pyris software. Measurements were carried out at a heating rate of 10 °C/min under a nitrogen purge. T_g was taken at one-half C_p extrapolated. ^{1}H, ^{13}C, and ^{19}F NMR measurements were performed on a QE-300 NMR spectrometer with a Techmag upgrade or a JEOL ECA-500 NMR spectrometer. ^{1}H and ^{13}C NMR spectroscopy were performed on dilute solutions in $CDCl_3$ or DMSO-d_6 and referenced to tetramethylsilane at δ 0.00. ^{19}F NMR spectroscopy was performed on dilute solutions in DMSO-d_6. The ^{19}F chemical shifts were referenced to $CFCl_3$ at δ 0.00. Intrinsic viscosity measurements were performed with a Cannon-Ubbelohde viscometer in a 30 °C thermostat controlled water bath. Each data point was an average of at least three measurements. The intrinsic viscosity was taken as an average of the intercepts of the linear extrapolations of the reduced and inherent viscosities versus concentration plots. Average molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC) on a Viscotek GPCmax VE-2001 chromatograph equipped with Viscotek Model 270 Series differential viscometer/low angle laser light scattering detectors and a refractive index detector Model 3580. Elutions were performed with two ViscoGel I-Series columns (I-M and I-H) in series at 55 °C. Dimethylformamide (DMF) with ammonium acetate (0.02 M) was used as the eluent with a flow rate of 1 mL/min. Molecular weight data analysis was performed using OmniSec software. Matrix-assisted laser desorption/ionization-time-of-flight (MALDI-TOF) mass spectrometry was performed on a PerSeptive Biosystems Voyager DE instrument. Data Explorer software was used for data manipulation. The samples were prepared by depositing a 3:1:1 (by volume) mixture of a 1 mg/mL solution of polymer in DMSO, a 13.6 mg/mL solution of 1,8,9-anthracentriol (dithranol) in THF, and a 1 mg/mL solution of sodium trifluoroacetate in THF. The samples were dried *in vacuo*. Elemental analysis was performed by Huffman Laboratories (Golden, CO). The semiempirical calculations were performed with Spartan 04 software at the PM3 level.

Synthesis of 2,4-Difluoro-*N,N*-dimethylbenzenesulfonamide (1). 2,4-Difluorobenzenesulfonyl chloride (120.9 mmol, 25.71 g) was added to a 500 mL Erlenmeyer flask followed by 150 mL of dichloromethane. Dimethylamine (271.4 mmol, 47.05 g) was added to the flask with 200 mL of deionized water (DI H_2O). The mixture was stirred at room temperature for 3 days. The organic layer was separated, and the aqueous layer was extracted two times with dichloromethane. The combined organic layer was washed with 5% hydrochloric acid, water, 0.1 M sodium hydroxide solution, and water. The dichloromethane was removed by rotary evaporation, and the resulting oil crystallized upon cooling. The product was recrystallized twice from 65/35 ethanol/water and dried under vacuum overnight. Pure yield: 62%; mp: 30.1−31.2 °C. ^{1}H NMR ($CDCl_3$ with respect to TMS at 0.00, δ): 2.84 (s, 6H), 6.94−7.04 (m, 2H), and 7.85−7.93 (q, 1H). Elem. Anal. Calculated for $C_8H_9F_2NO_2S$: C, 43.43%; H, 4.11%; F, 17.18%; N, 6.33%; O, 14.46%, S, 14.49%. Found: C, 43.56%; H, 4.15%; F, 17.18%; N, 6.50%; S, 14.79%.

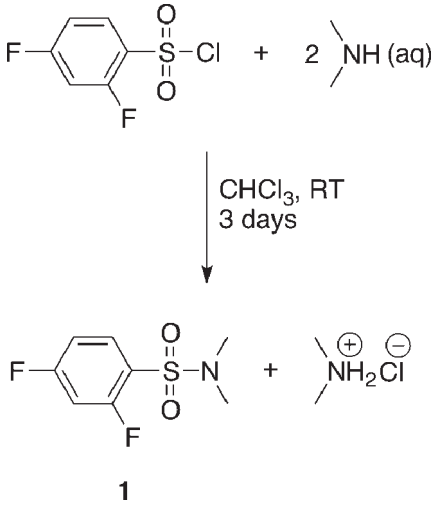
Synthesis of 2,4-(4-*tert*-Butylphenoxy)-*N,N*-dimethylbenzenesulfonamide (2). **1** (4.521 mmol, 1.000 g), 4-*tert*-butylphenol (9.107 mmol, 1.368 g), potassium carbonate (6.79 mmol, 0.939 g), DMPU or NMP (9 mL), and toluene (10 mL) were added to a dry, two-neck 50 mL round-bottom flask. The flask was equipped with a stirbar, a Dean−Stark trap, a condenser, and a nitrogen inlet. Water was azeotropically distilled with the toluene at 140 °C for about 6 h in a thermostat controlled oil bath. The temperature of the oil bath was increased to 165 °C for 20 h. The reaction was monitored by thin layer chromatography (TLC) in 80/20 hexanes/ethyl acetate. The completion of the reaction was determined by the formation of a single product spot and the disappearance of **1**. The product (**2**) was precipitated in 300 mL of DI H_2O. The off-white precipitate was extracted with dichloromethane, washed with DI H_2O four times, and dried over magnesium sulfate. The solvent was removed by rotary evaporation. The product was purified by flash chromatography in 80/20 hexanes/ethyl acetate and then recrystallized from 80/20 ethanol/water. The product was dried under vacuum overnight. Pure yield: 74%; mp: 114.0−118.6 °C. ^{1}H NMR ($CDCl_3$ with respect to TMS at 0.00, δ): 1.31−1.32 (d, 18H), 2.89 (s, 6H), 6.52−6.57 (m, 2H), 6.91−7.01 (dd, 4H), 7.34−7.39 (t, 4H), and 7.86−7.89 (d, 1H). Elem. Anal. Calculated for $C_{28}H_{35}NO_4S$: C, 69.82%; H, 7.32%; N, 2.91%; O, 13.29%, S, 6.66%. Found: C, 70.01%; H, 7.31%; N, 2.96%; S, 6.79%.

Polymerization. All polymerizations were carried out in a similar manner. The following is a detailed example polymerizing **1** with bisphenol A. **1** (9.051 mmol, 2.002 g) was weighed into a dry two-neck 50 mL round-bottom flask. The flask was equipped with a stirbar, a Dean−Stark trap, a condenser, and a nitrogen inlet. The flask was charged with bisphenol A (9.051 mmol, 2.066 g), potassium carbonate (13.62 mmol, 1.882 g), NMP (13 mL), and toluene (10 mL). Water was azeotropically removed with the toluene at 140 °C for 6 h, after which the toluene was removed. The temperature was increased to 165 °C for 16 h. The viscous mixture was diluted with 25 mL of NMP and precipitated in methanol. The polymer (**3**) was boiled in DI H_2O for 30 min then dried under vacuum at 80 °C overnight. Polymerizations using 4,4′-biphenol, bisphenol AF, and hydroquinone to produce polymers **4**, **5**, and **6**, respectively, were performed in a similar manner.

RESULTS AND DISCUSSION

A significant amount of research on new activating groups for nucleophilic aromatic substitution polymerization has been done to design the properties of poly(aryl ether)s for applications. The incorporation of a variety of functional groups into the backbone has produced polymers with a range of unique properties.[7,9,11,13,37−40]

Scheme 1. Monomer Synthesis



1

Polymers with pendent functionality offer an alternative method to produce desired properties. In order to incorporate the pendent functional group in poly(aryl ether)s, a separate functionality is typically included in one of the monomers in addition to the activating group or the polymer is functionalized post-polymerization. These routes can lead to side reactions and a lack of control over functionalization. Also, the polymers contain multiple functionalities that can have an adverse effect on the properties of the polymers. Incorporating a sulfonamide to activate two positions on the same aromatic ring activates the aryl fluorides for substitution and incorporates the desired functionality into the polymer without interfering with the polymerization.

In order to study the activating nature of the sulfonamide moiety, a sulfonamide functional difluorobenzene (**1**) was synthesized through a simple substitution reaction (Scheme 1). The reaction was carried out in an interfacial mixture, from which the product was easily recovered and purified by recrystallization. The structure of **1** was confirmed by ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy, mass spectrometry, and elemental analysis.

The effectiveness of an electron-withdrawing group to activate aryl fluorides toward nucleophilic substitution has been studied by two methods, each focusing on *para*-fluoro compounds. The first method is computational and examines the net charge on the *ipso* carbon as a measure of the potential reactivity via a S_NAr mechanism, with a larger positive charge at the *ipso* carbon indicating an increased reactivity with a nucleophile in a S_NAr mechanism. Semiempirical molecular orbital calculations have been used to gauge reactivity of activated aryl fluorides.[1,2,40,41] The second method to assess the activating nature of an electron-withdrawing group for the nucleophilic displacement of aryl fluorides is through NMR spectroscopy. The ^{1}H, ^{13}C, and ^{19}F NMR chemical shifts are used to estimate reactivity based on correlations derived from known activated molecules for S_NAr polymerization.

Semiempirical calculations were performed at the PM3 level to estimate the reactivity of **1** with nucleophiles. The results are shown in Table 1 along with literature results[1,2] for other aryl fluorides. Bis(4-fluorophenyl) sulfone and 4,4′-difluorobenzophenone are compared as commonly used monomers for polymerization. Bis(4-fluorophenyl)amide is compared as a similar functional group. Fluorobenzene is included to depict an unreactive molecule. The charge at the carbon *para* to the sulfonamide was found to be 0.144. This value is significantly higher than strongly activated monomers such as sulfone or ketone,[2] suggesting that the sulfonamide is highly activating toward substitution.

Table 1. Semiempirical Calculations and NMR Spectroscopy Results for 1 and Other Aryl Fluorides

compound	charge at *ipso* C	charge at F	^{13}C NMR ($CDCl_3$)	^{19}F NMR (DMSO-d_6)
1 (C−F *ortho* to sulfonamide)	0.199	−0.078	159.93	−104.82
1 (C−F *para* to sulfonamide)	0.144	−0.080	165.79	−103.08
bis(4-fluorophenyl) sulfone	0.117[a]	−0.085[a]	165.30[a]	−104.08[a]
4,4′-difluorobenzophenone	0.096[a]	−0.088[a]	165.27[b]	−106.01[b]
bis(4-fluorophenyl)amide	0.095[a]	−0.086[a]	164.04[a]	−108.55[a]
4-fluorobenzene	0.065[a]	−0.093[a]	162.29[a]	−112.77[a]

[a] Data taken from ref 2. [b] Data taken from ref 1.

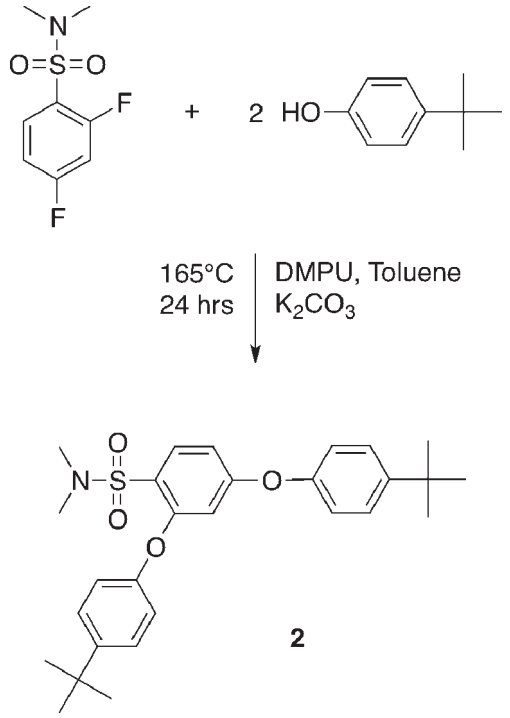
NMR chemical shift values have been shown to correlate well with the reactivity of aryl fluorides with respect to electron-withdrawing groups. The chemical shift of a proton *ortho* to a substituent can be used to estimate the inductive electron-withdrawing capabilities.[42] ^{1}H NMR spectroscopy of **1** reveals a chemical shift of δ 7.89 for the proton *ortho* to the sulfonamide, suggesting the monomer will have a reactivity similar to that of 4,4′-difluorobenzophenone, which has a shift of δ 7.9.[42] Although ^{1}H NMR spectroscopy directly explores the electron-withdrawing character of a moiety, it is an indirect method of examining the effect of an electron-withdrawing group on the reaction sites of a monomer. A more direct probe of the reaction site is ^{13}C NMR spectroscopy. ^{13}C NMR spectroscopy of **1** reveals the carbon *para* to the sulfonamide to have a chemical shift of δ 165.79, indicating it is more activated than sulfone (δ 165.30) and ketone (δ 165.27).[1] ^{19}F NMR also suggests that the *para* position is activated for polymerization with a chemical shift of δ −103.08. This value is similar to that found for bis-(4-fluorophenyl) sulfone (δ −104.08).[1] ^{1}H, ^{13}C, and ^{19}F NMR results all suggest that **1** is activated for S_NAr polymerization. Studies of the reactive site *ortho* to activating groups have not been explicitly investigated for comparison. In the case of **1**, the *ortho* site is assumed to be reactive because of the strong activation estimated for substitution at the *para* position.

The reactivity of **1** with phenolic nucleophiles was examined through a model reaction with 4-*tert*-butylphenol in DMPU or NMP as a solvent using potassium carbonate as a weak base (Scheme 2). Poly(aryl ether)s are commonly synthesized using a weak base to generate the nucleophile *in situ*.[7,11,13−15,38,43,44] Thin layer chromatography was used to monitor the reaction. A single product was formed after 24 h at 165 °C, indicating a complete reaction. The product was purified and identified by ^{1}H NMR, mass spectrometry, and elemental analysis. The complete conversion of **1** in a short amount of time and at a moderate temperature suggests that **1** is suitable for S_NAr polymerization.

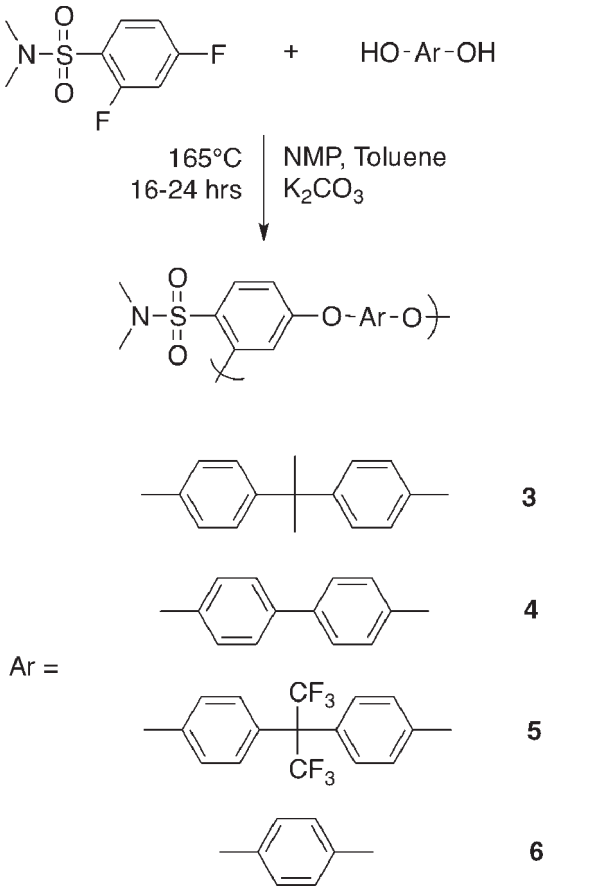
The polymerization of **1** with various bisphenols is depicted in Scheme 3 following the same reaction conditions used in the model reaction. NMP was preferred over DMPU due to solubility issues. A highly viscous solution indicative of high molecular weight polymer was formed within 16−24 h at 165 °C. Polymers formed from bisphenol A and bisphenol AF exhibit partial solubility in tetrahydrofuran and chloroform and complete solubility in DMF, DMSO, and NMP. The polymers

dx.doi.org/10.1021/ma201154b |*Macromolecules* 2011, 44, 6717–6723

Scheme 2. Synthesis of Model Compound 2



Scheme 3. Polymerization of 1 with Various Bisphenols



incorporating 4,4′-biphenol and hydroquinone were soluble in DMF, DMSO, and NMP.

^{1}H NMR spectroscopy was used to characterize the repeat unit structure of each of the polymers. The spectrum obtained from polymer **3** in DMSO-d_6 is shown as an example in Figure 1, and the chemical shift assignments are depicted in the figure.

Average molecular weights were measured by gel permeation chromatography using low angle light scattering detection. Each of the polymerizations produced high molecular weight polymers with varying amounts of low molecular weight material as depicted in the GPC chromatograms (Figure 2). The average molecular weights and polydispersities reported are determined by selecting the entire sample (Table 2). The peaks at high elution volume are presumably low molecular weight cyclics and are produced to varying extent depending on the bisphenol monomer used. The polymerization using 4,4-biphenol (**4**) and hydroquinone (**6**) result in larger amount of low molecular weight material. 4,4′-Biphenol and hydroquinone are very rigid molecules due to the aromatic rings and lack of free bond rotation. The rigidity of the monomer coupled with the *meta* linkage in the activated monomer is presumed to produce a significant concentration of low molecular weight cyclics, particularly a cyclic dimer, thereby broadening the polydispersity.

The MALDI-TOF mass spectra for each of the polymers (Figure 3) exhibit a series of peaks with molecular weights matching cyclic species, suggesting that the 2,4 substitution influences the formation of cyclics. A similar phenomenon has been seen with difluorobenzophenone, where the 2,4-difluorobenzophenone produced a larger amount of cyclics than other isomers.[20] In the spectrum for polymer **4**, the peak corresponding to the repeat unit trimer is missing. In the spectra for both polymer **4** and polymer **6**, the distribution is favored toward the lower cyclics. This data supports the conclusion that the larger low molecular weight peak in the GPC chromatograms for these

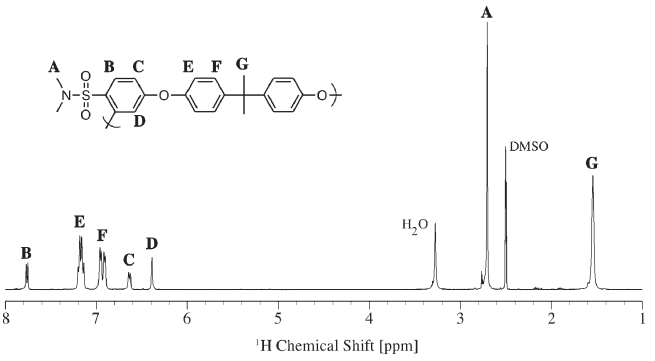


Figure 1. ^{1}H NMR spectrum of polymer **3** in DMSO-d_6.

two polymers is due to favored cyclic formation because of the rigidity of the comonomer.

The polymers were melt-pressed or solution cast into creasable thin films. Solution viscometry was used to measure the molecular weight to corroborate the high molecular weight measured for polymer **3**. It was hypothesized that the unusually high molecular weight could be due to aggregation of chains. The viscosity was measured using a Cannon-Ubbelohde viscometer at a series of concentrations of each polymer. The reduced and inherent viscosities were calculated and plotted against concentration. The linear data were extrapolated to zero concentration, and the intrinsic viscosity was taken as the average of the two

dx.doi.org/10.1021/ma201154b |*Macromolecules* 2011, 44, 6717–6723

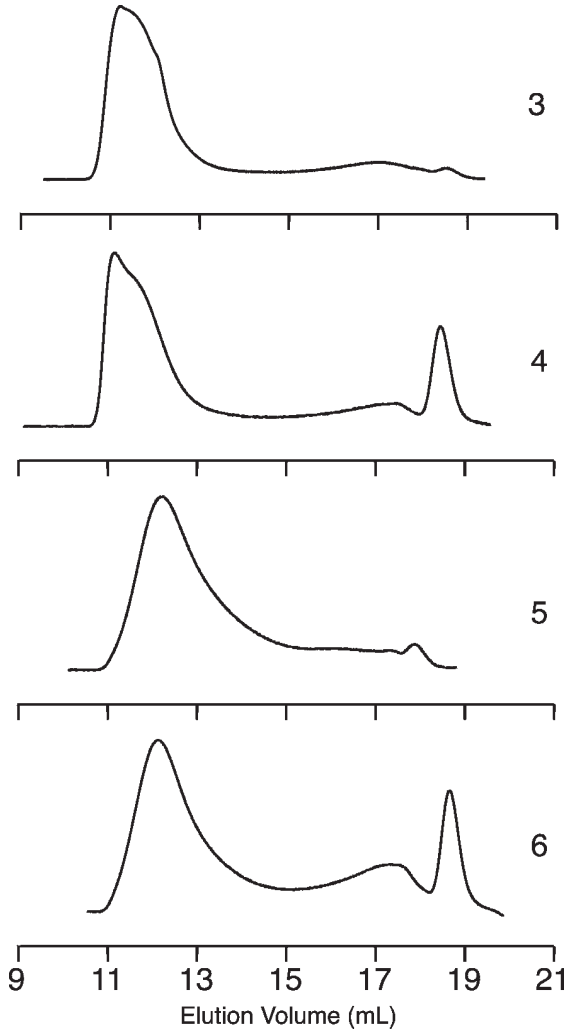


Figure 2. Gel permeation chromatograms of poly(aryl ether sulfonamide)s.

Table 2. Characterization Results for Poly(aryl ether sulfonamide)s

polymer	M_n[a]	M_w[a]	M_w/M_n	$[\eta]$ (dL/g)[b]	T_g (°C)[c]	TGA 5% loss[c]
3	109 000	446 000	4.1	0.99	163	435
4	20 100	207 000	10.3	0.30	199	417
5	34 900	82 900	2.4	0.27	187	442
6	7 170	74 400	10.4	0.21	169	398

[a] Measured by GPC with light scattering detection. [b] Measured in DMF at 30 °C. [c] Measured under a nitrogen atmosphere.

intercepts. Intrinsic viscosities for all four polymers are shown in Table 2. The plots of reduced and inherent viscosities versus concentration were very linear with R^2 values of 0.999 and 0.993, respectively (Figure 4). The linearity suggests that there is no aggregation and the high viscosity is due to the high molecular weight of the polymer. The data for the other polymers were similarly linear and the intrinsic viscosities correlated well with the molecular weight values determined by light scattering.

The thermal properties of the polymers were measured by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) (Table 2). The polymers exhibited moderately

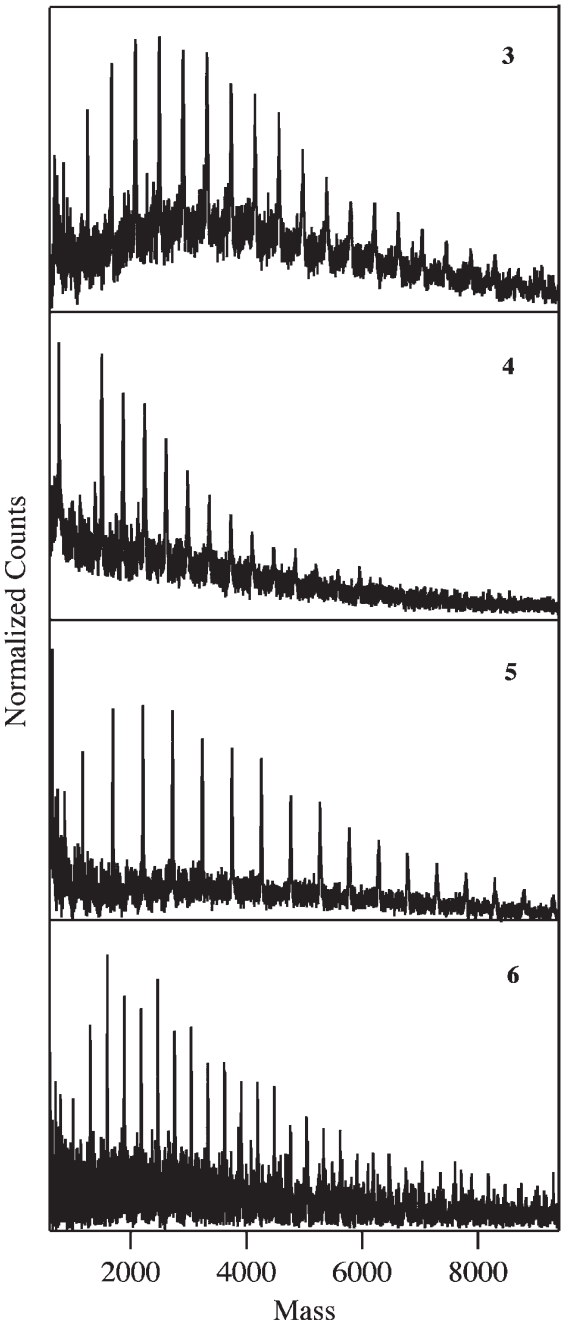


Figure 3. MALDI-TOF mass spectra of poly(aryl ether sulfonamide)s.

high glass transition temperatures (T_g) in the range of 163−199 °C depending on the bisphenol used. Polymer **4** exhibited the highest T_g at 199 °C, and this can be attributed to the rigidity imparted by the 4,4′-biphenol in the backbone. Polymer **5** also displayed a higher T_g than polymers **3** and **6** due to the stronger interchain interactions of the $-CF_3$ groups. The thermal stabilities of these polymers were determined using dynamic TGA in a nitrogen atmosphere at a heating rate of 10 °C/min (Figure 5). All of the polymers exhibited good thermal stability with 5% weight loss values from 398 to 443 °C depending on the bisphenol used in the polymerization (Table 2). Polymers **3** and **4** show some weight loss starting around 200 °C. This can be attributed to residual

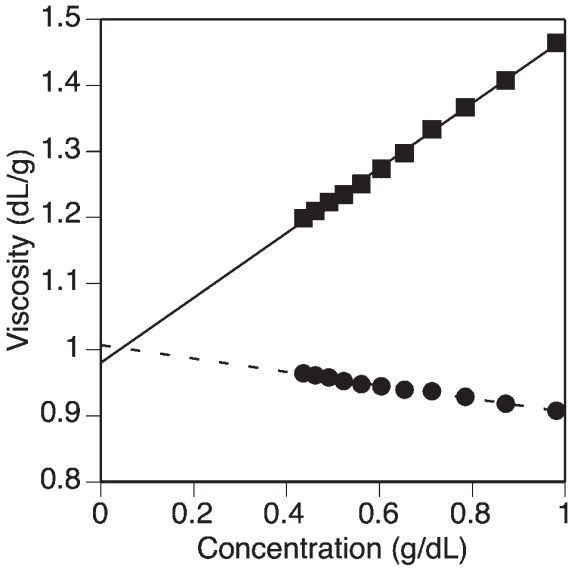


Figure 4. Plot of reduced viscosity (■) and inherent viscosity (●) versus concentration measured in DMF at 30 °C. Linear fits of reduced viscosity (—) and inherent viscosity (- - -) are also plotted.

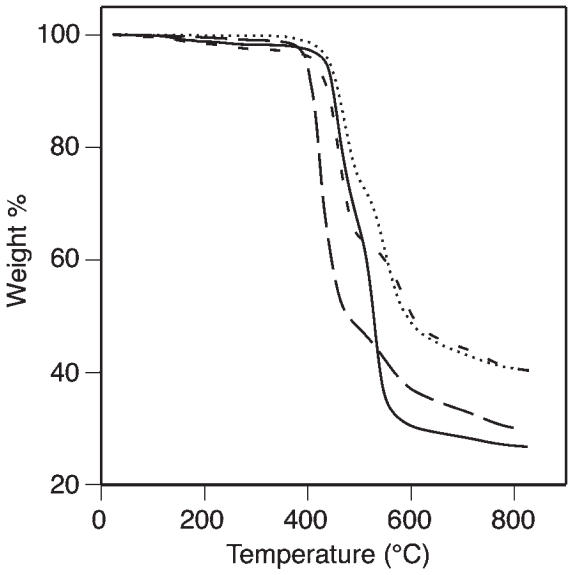


Figure 5. Thermogravimetric analysis of polymers **3** (—), **4** (- - -), **5** (· · ·), and **6** (— —) in a nitrogen atmosphere at a heating rate of 10 °C/min.

NMP solvent that was difficult to remove from the very high molecular weight polymers.

CONCLUSIONS

This research confirms that sulfonamides activate aryl fluorides for substitution in S_NAr polymerization. The activation allowed quantitative substitution at both the *ortho* and *para* position, producing pendent sulfonamide polymers. The incorporation of different bisphenols introduced compositional variety into the high molecular weight polymers that were formed. The materials demonstrated moderately high T_g's from 163 to 199 °C, depending on the bisphenol used in the polymerization. Good thermal stabilities were shown for each polymer with 5% weight loss values at or above 400 °C.

AUTHOR INFORMATION

Corresponding Author
*E-mail: dknauss@mines.edu.

ACKNOWLEDGMENT

This work was supported by the Renewable Energy Materials Research Science and Engineering Center funded by the National Science Foundation (DMR-0820518). The NMR spectroscopy was possible through an NSF MRI grant (CHE-0923537).

REFERENCES

(1) Carter, K. R. *Macromolecules* **1995**, *28* (19), 6462–6470.
(2) Lozano, A. E.; Jimeno, M. L.; de Abajo, J.; de la Campa, J. G. *Macromolecules* **1994**, *27* (24), 7164–7170.
(3) Attwood, T. E.; Barr, D. A.; Feasey, G. G.; Leslie, V. J.; Newton, A. B.; Rose, J. B. *Polymer* **1977**, *18* (4), 354–358.
(4) Johnson, R. N.; Farnham, A. G.; Clendinning, R. A.; Hale, W. F.; Merriam, C. N. *J. Polym. Sci., Part A-1: Polym. Chem.* **1967**, *5* (9), 2375–2398.
(5) Wang, F.; Hickner, M.; Kim, Y. S.; Zawodzinski, T. A.; McGrath, J. E. *J. Membr. Sci.* **2002**, *197* (1−2), 231–242.
(6) Shao, K.; Zhu, J.; Zhao, C.; Li, X.; Cui, Z.; Zhang, Y.; Li, H.; Xu, D.; Zhang, G.; Fu, T.; Wu, J.; Na, H.; Xing, W. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47* (21), 5772–5783.
(7) Hedrick, J. L. *Macromolecules* **1991**, *24* (3), 812–813.
(8) Lucas, M.; Hedrick, J. *Polym. Bull.* **1992**, *28* (2), 129–133.
(9) Gauderon, R.; Plummer, C. J. G.; Hilborn, J. G.; Knauss, D. M. *Macromolecules* **1998**, *31* (2), 501–507.
(10) Knauss, D. M.; Edson, J. B. *Polymer* **2006**, *47* (11), 3996–4003.
(11) Edson, J. B.; Knauss, D. M. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42* (24), 6353–6363.
(12) Robb, M. J.; Knauss, D. M. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47* (9), 2453–2461.
(13) Bernal, D. P.; Bankey, N.; Cockayne, R. C.; Fossum, E. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40* (10), 1456–1467.
(14) Lin, Q.; Long, T. E. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38* (20), 3736–3741.
(15) Smith, C. D.; Grubbs, H.; Webster, H. F.; Gungor, A.; Wightman, J. P.; McGrath, J. E. *High Perform. Polym.* **1991**, *3* (4), 211–229.
(16) Kaiti, S.; Himmelberg, P.; Williams, J.; Abdellatif, M.; Fossum, E. *Macromolecules* **2006**, *39* (23), 7909–7914.
(17) van Beek, D.; Fossum, E. *Macromolecules* **2009**, *42* (12), 4016–4022.
(18) Ding, J.; Day, M. *Macromolecules* **2006**, *39* (18), 6054–6062.
(19) Miller, J.; Williams, V. A. *J. Am. Chem. Soc.* **1954**, *76* (21), 5482–5484.
(20) Kricheldorf, H. R.; Vakhtangishvili, L.; Schwarz, G.; Prosenc, M. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43* (24), 6233–6246.
(21) Kricheldorf, H. R.; Schwarz, G.; Erxleben, J. *Makromol. Chem.* **1988**, *189* (10), 2255–2267.
(22) Kricheldorf, H. R.; Garaleh, M.; Schwarz, G. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41* (23), 3838–3846.
(23) Kricheldorf, H. R.; Meier, J.; Schwarz, G. *Makromol. Chem., Rapid Commun.* **1987**, *8* (11), 529–534.
(24) Matsuo, S.; Murakami, T.; Takasawa, R. US Patent 4,703,104, 1987.
(25) Matsuo, S.; Murakami, T.; Takasawa, R. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31* (13), 3439–3446.
(26) Sumner, M. J.; Harrison, W. L.; Weyers, R. M.; Kim, Y. S.; McGrath, J. E.; Riffle, J. S.; Brink, A.; Brink, M. H. *J. Membr. Sci.* **2004**, *239* (2), 199–211.

(27) Takekoshi, T.; Wirth, J. G.; Heath, D. R.; Kochanowski, J. E.; Manello, J. S.; Webber, M. J. *J. Polym. Sci., Part A: Polym. Chem.* **1980**, *18* (10), 3069–3080.
(28) Kubrakova, I. V.; Formanovsky, A. A.; Mikhura, I. V. *Mendeleev Commun.* **1999**, *9* (2), 65–66.
(29) Richman, J. E.; Atkins, T. J. *J. Am. Chem. Soc.* **1974**, *96* (7), 2268–2270.
(30) Fukuyama, T.; Jow, C.-K.; Cheung, M. *Tetrahedron Lett.* **1995**, *36* (36), 6373–6374.
(31) Li, Z.; van Lier, J.; Leznoff, C. C. *Can. J. Chem.* **1999**, *77* (1), 138–145.
(32) Heppolette, R. L.; Miller, J. *J. Chem. Soc.* **1956**, 2329–2334.
(33) Herath, M. B.; Creager, S. E.; Rajagopal, R. V.; Geiculescu, O. E.; DesMarteau, D. D. *Electrochim. Acta* **2009**, *54* (24), 5877–5883.
(34) Quattropani, A.; Dorbais, J.; Covini, D.; Pittet, P.-A.; Colovray, V.; Thomas, R. J.; Coxhead, R.; Halazy, S.; Scheer, A.; Missotten, M.; Ayala, G.; Bradshaw, C.; De Raemy-Schenk, A.-M.; Nichols, A.; Cirillo, R.; Tos, E. G.; Giachetti, C.; Golzio, L.; Marinelli, P.; Church, D. J.; Barberis, C.; Chollet, A.; Schwarz, M. K. *J. Med. Chem.* **2005**, *48* (24), 7882–7905.
(35) Serra-Muns, A.; Soler, R.; Badetti, E.; de Mendoza, P.; Moreno-Mañas, M.; Pleixats, R.; Sebastián, R. M.; Vallribera, A. *New J. Chem.* **2006**, *30* (11), 1584–1594.
(36) Sturm, K.; Muschaweck, R.; Hropot, M. *J. Med. Chem.* **1983**, *26* (8), 1174–1187.
(37) Hedrick, J. L.; Labadie, J. W. *Macromolecules* **1988**, *21* (6), 1883–1885.
(38) Hilborn, J. G.; Labadie, J. W.; Hedrick, J. L. *Macromolecules* **1990**, *23* (11), 2854–2861.
(39) Kim, S. Y.; Labadie, J. W. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1991**, *32* (1), 164–165.
(40) Yeomans, K. A.; Hay, A. S. *Polym. Mater. Sci. Eng.* **1993**, *69*, 240–241.
(41) Strukelj, M.; Hamier, J.; Elce, E.; Hay, A. S. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32* (1), 193–198.
(42) Hedrick, J. L.; Labadie, J. W. *Macromolecules* **1990**, *23* (6), 1561–1568.
(43) Hedrick, J.; Twieg, R.; Matray, T.; Carter, K. *Macromolecules* **1993**, *26* (18), 4833–4839.
(44) Twieg, R.; Matray, T.; Hedrick, J. L. *Macromolecules* **1996**, *29* (23), 7335–7341.