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Poly(aryl ether sulfide)s by sulfide-activated nucleophilic aromatic substitution polymerization

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Abstract

Poly(aryl ether sulfide)s have been produced by nucleophilic aromatic substitution with phenoxide nucleophiles bisphenol A and bisphenol AF, and the activated arylfluorides bis(4-fluorophenyl)sulfide and 2,7-difluorothianthrene. The resulting polymers are thermally stable, amorphous materials that have been characterized by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and gel permeation chromatography (GPC). Moderate molecular weights have been achieved, representative of greater than 98% conversion of arylfluorides. The poly(aryl ether thianthrene)s are flame resistant and self extinguish within 0.2 s upon removal from a flame source. TGA of the poly(aryl ether thianthrene)s in an inert atmosphere result in a char yield greater than 50% at 750 °C. The flame resistant properties are more effectively modeled by TGA in an inert atmosphere as compared to TGA in an air atmosphere. The poly(aryl ether thianthrene)s are found to have high refractive index values, 1.61–1.70, depending on wavelength and bisphenol composition.

Keywords: Poly(aryl ether)s; Synthesis; Nucleophilic aromatic substitution

1. Introduction

Professor James McGrath has made many valuable contributions to the area of polymer science and engineering over his career. One area in which he has made a sizable impact is in the class of polymers known as poly(aryl ether)s, where he has contributed to the development of synthesis techniques, the characterization of polymer properties, and materials design for application with more than 150 publications. Some of the more noteworthy accomplishments include the development of the potassium carbonate ‘weak base’ method of synthesis [1], the use of phenylphosphine oxide activated monomers and the characterization of the resulting polymers [2–11], the production of high temperature thermosets from reactive oligomers [9,11–14], and most recently in the design of activated sulfonate monomers for the synthesis of well-defined sulfonic acid functionalized poly(aryl ether sulfone)s and poly(aryl sulfide sulfone)s for use as improved PEM fuel cell membranes [15–26].

Former McGrath students have followed in this vein and have also contributed to the field of poly(aryl ether)s with some of their work described here. Hedrick has investigated numerous electron withdrawing heterocylic and other groups to activate aryl fluorides for substitution by phenoxide nucleophiles [27–37]. DeSimone has researched poly(aryl ether)s with kinks in the polymer chain from 2,5-thiophene units in the monomers [38–41]. Mohanty has studied the activation of aryl fluorides by diazo groups, the synthesis of block copolymers of poly(aryl ether)s, and competitive radical reactions [42–48]. We have also been active in this area through the investigation of azomethines as activating groups [49] and through continuing recent research on the activation of aryl fluorides for nucleophilic aromatic substitution by using groups that are not strong electron withdrawing groups, but which can activate the substitution by electron accepting means [50,51].

This paper will describe some of the recent results obtained in our group on the activation of aryl fluorides for substitution by nucleophilic aromatic substitution polymerization and the material properties of the polymers. While some of the results are preliminary, conclusions can be drawn and the continued direction of the research outlined.

2. Experimental

All commercially available solvents and reagents were obtained from Aldrich and used as received unless otherwise indicated. Toluene (HPLC grade) was washed with cold concentrated sulfuric acid, three times with water, dried over calcium chloride, and then distilled from sodium metal under

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an argon atmosphere before use. 1,3-Dimethyl-3,4,5,6-tetrahydro-2-(1*H*)-pyrimidinone (DMPU) (98%) was distilled from calcium hydride at reduced pressure. *para*-Cresol (99%) was distilled at reduced pressure. Bisphenol A (97%) was recrystallized three times from toluene and dried in a vacuum oven at 80 °C over two days. Hexafluorobisphenol A (bisphenol AF) (97%) was recrystallized from a toluene/ethyl acetate mixture (95/5) and was then sublimed under reduced pressure. 4,4′-Biphenol was recrystallized twice from ethanol and dried in a vacuum oven at 80 °C. Potassium carbonate was dried for 24 h at 110 °C in a vacuum oven.

2.1. 2,7-Difluorothianthrene and poly(aryl ether thianthrene)s

The synthesis of 2,7-difluorothianthrene and its polymerization with bisphenol A, bisphenol AF, and biphenol to make poly(aryl ether thianthrene)s has been recently described [51].

2.2. Bis(4-fluorophenyl)sulfoxide

Aluminum chloride (60.6 g, 0.45 mol) and fluorobenzene (100 mL) were added to a 250 mL 3-neck flask containing a magnetic stir bar. A 25 mL addition funnel, an argon inlet adapter, and a condenser with an outlet that led to a KOH/water solution were attached to the 3-necks. Thionyl chloride (15 mL, 0.21 mol) was added to the addition funnel and then slowly introduced to the stirring reaction mixture. HCl that was produced was swept to the KOH/water solution by a constant flow of argon. The thionyl chloride was introduced over 1.5 h and the reaction mixture was then heated to reflux for 4 h. The reaction mixture was poured onto 300 g of crushed ice. One hundred millilitre of methylene chloride was added and the organic layer was separated and extracted with 100 mL of a 10% sodium bicarbonate solution, followed by two washings with 100 mL portions of water. Rotary evaporation of the organic extract yielded 32.5 g of a pale yellow oil that crystallized overnight. Recrystallization twice from hexanes yielded 28.8 g (59% yield) of white crystals. Mp: 46.6–47.0 °C (literature melting point [52] 50.5 °C).

2.3. Bis(4-fluorophenyl)sulfide

Bis(4-fluorophenyl)sulfoxide was reduced following a modified procedure of that reported in the literature for polymeric sulfoxides [53,54]. Bis(4-fluorophenyl)sulfoxide (20.0 g, 0.084 mol) and tetrabutylammonium iodide (37.2 g, 0.10 mol) were introduced into a 1000 mL 2-neck round bottom flask containing a magnetic stir bar and equipped with a condenser. Six hundred millilitre of chloroform were added and the second neck of the flask was sealed with a rubber septum. The contents were put under a slight positive pressure of argon and the contents were heated to 50 °C using an external water bath. Oxalyl chloride (11.6 mL, 0.092 mol) was introduced over the course of 20 min through a syringe. Gas was evolved from the exothermic reaction and the mixture turned a dark red color. The reaction was allowed to stir for 2 h at 50 °C and then overnight at room temperature. The solution was washed twice with 200 mL portions of water, and the chloroform removed by rotary evaporation. The resulting 18 g of yellow oil was fractionally distilled three times at 70–80 °C and 100–300 mTorr. ^{1}H NMR: [$CDCl_3$ relative to tetramethylsilane (TMS) at 0.00]: δ 7.22–7.26 (m, 4H) 6.90–6.94 (m, 4H); ^{13}C NMR: [$CDCl_3$ relative to TMS at 0.00]: δ 162.24, 133.06, 131.30, 116.43.

2.4. Model compound

A 50-mL three-necked round bottom flask fitted with an argon inlet, magnetic stir bar, and Dean–Stark trap with an attached condenser was charged with bis(4-fluorophenyl)sulfide (2.18 g, 9.83 mmol), *p*-cresol (2.44 g, 22.6 mmol) and anhydrous K_2CO_3 (3.17 g, 22.6 mmol) and was washed into the flask with 20 mL DMPU and 10 mL dry toluene. The reaction flask was heated to 145–155 °C and water formed during the phenoxide formation was removed to the Dean–Stark trap by azeotropic distillation with toluene. After 4 h, the toluene was removed from the Dean–Stark trap and 10 mL of dry toluene was added to the reaction mixture to ensure complete dehydration of the system. After 2 more hours and toluene removal from the trap, the reaction was heated to 165 °C for 14 h, at which time thin layer chromatography (TLC) with hexanes/ethyl acetate (80/20) showed complete conversion of bis(4-fluorophenyl)sulfide to the formation of a single product. The reaction mixture was added to 250 mL of a 10% potassium carbonate solution and the product extracted into methylene chloride. The organic fraction was further extracted with potassium carbonate solution and two 100 mL portions of water, dried over magnesium sulfate, and concentrated by rotary evaporation to yield a light brown oil that crystallized overnight. Recrystallization from hexanes yielded 3.20 g of light brown crystals (81.7%). ^{1}H NMR: [$CDCl_3$ relative to TMS at 0.00]: δ 7.25–7.28 (d, 4H) 7.08–7.11 (d, 4H), 6.87–6.91 (m, 8H), 2.31(s, 6H); ^{13}C NMR: [$CDCl_3$ relative to TMS at 0.00]: δ 157.43, 154.27, 133.30, 132.70, 130.34, 129.45, 119.35, 118.88, 20.69. Mp: 108.4–109.9 °C

2.5. Poly(aryl ether sulfide)s

Polymerization of the bis(4-fluorophenyl)sulfide was performed with bisphenol A and with bisphenol AF by a similar procedure. Details of the bisphenol A polymerization are provided. The bis(4-fluorophenyl)sulfide (1.459 g, 6.565 mmol) was weighed into a three-necked 50-mL round bottom flask and was followed by bisphenol A (1.499 g, 6.565 mmol) and 12 mL of DMPU. An argon inlet, mechanical overhead stirrer, and a 6-mL Dean–Stark trap and condenser were attached to the flask. Potassium carbonate (1.82 g, 13.1 mmol) was added to the mixture followed by 10 mL of dry toluene. The flask was heated with an external oil bath to 150 °C and toluene was removed to the Dean–Stark trap. After 3 h, the toluene was removed from the trap and 10 mL of dry toluene was added to the flask. After another 3 h, the toluene was removed from the trap and the oil bath temperature was increased to 185 °C for 18 h. An increase in viscosity was observed and the cooled polymer solution was precipitated into 200 mL of methanol containing 1 mL of acetic acid. The precipitated polymer was filtered and washed with more methanol, then boiled in water to remove salts, filtered and dried under vacuum to a constant weight. Yield of polymer was 2.6 g (96%).

2.6. Characterization

Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC) on a Hewlett–Packard model 1084B liquid chromatograph equipped with a Waters R401 refractive index detector. Elutions were carried out with two Hewlett–Packard PLgel 5-µm mixed-D columns at ambient temperature with tetrahydrofuran (THF) as a solvent at a flow rate of 1.0 mL/min. The molecular weights were determined relative to polystyrene standards (Polysciences, Inc.). Glass-transition temperatures (T_g's) were determined by differential scanning calorimetry (DSC) with a Perkin–Elmer DSC-1 running Pyris software. Heating rates were 10 °C/min and measurements were carried out under nitrogen purge. T_g was taken as the midpoint of the change in slope of the baseline. Thermal stabilities of the polymers were determined by thermogravimetric analysis (TGA) using a Seiko TGA. Heating rates were 10 °C/min and scans were carried out under an air or helium atmosphere. ^{1}H and ^{13}C NMR spectroscopy was performed with a Chemagnetics CMX Infinity 400 NMR spectrometer. ^{1}H and ^{13}C NMR measurements were performed in $CDCl_3$ and are reported relative to TMS as a reference. Film samples for flammability tests were cast from 5 wt% solutions in THF and were thoroughly dried under vacuum at 80 °C.

3. Results and discussion

Poly(aryl ether)s are an important class of high performance polymers [55]. The polymers have good thermal and oxidative stability along with high glass transitions temperatures or melting temperatures, making them useful for high temperature applications. Many compositionally different polymers have been produced by varying the monomers that make up the backbone yielding materials with a range of different thermal and mechanical properties.

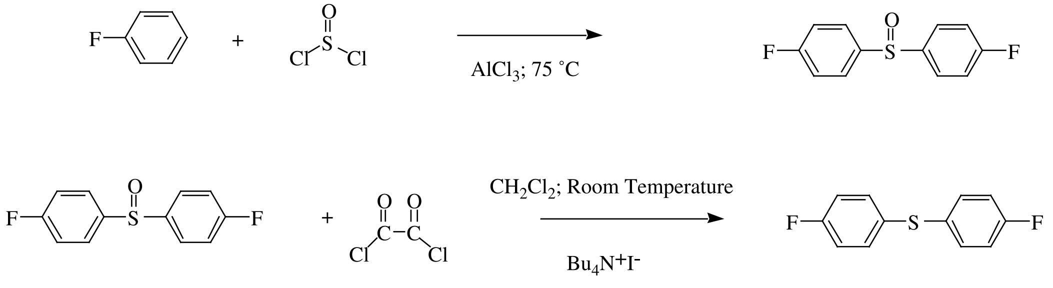
The ether linkage in the backbone of the polymer can be most readily produced by nucleophilic aromatic substitution through a S_NAr mechanism. This mechanism typically requires an electron withdrawing group that can stabilize a Meisenheimer-like sigma complex, which is produced as an intermediate [56]. The original research on the synthesis of poly(aryl ether)s utilized sulfone, ketone, sulfoxide, azo, nitro, and oxadiazole groups as electron withdrawing moieties to activate either fluoro or chloro substitution [57]. More recent research has been directed toward the identification and use of new activated monomers for nucleophilic aromatic substitution polymerization. Many different groups, all of which can be considered strong electron withdrawing groups, have been identified as capable of activating an aryl halide for nucleophilic aromatic substitution by a S_NAr mechanism. Examples of some of these activating groups include azomethines [49], imides [58], benzoxazoles [29], azo groups [47], amides [32], *o*-benzoylbenzene [59], and phenylphosphine oxide [2].

The extent of the electron withdrawing character of the activating groups can be characterized by nuclear magnetic resonance (NMR), or by modeling the charge density at the reaction site through semi-empirical molecular orbital calculations [60–62]. Tables of charge density for some known activated monomers have been produced. Correlation analysis by Hammet σ–ρ plots have also been done to determine reactivity [56,63]. As σ values for a variety of substitutents are available [64,65], the evaluation can be a simple task. σ values that indicate a significant electron withdrawing character are proposed to indicate a good activating group [33]. There are limitations in the methods for determining reactivity. Each of the methods investigates the inductive electron withdrawing effects of the activating group, but does not adequately measure the stabilizing ability of the Meisenheimer complex intermediate [27]. Therefore, each of the described methods could fail to indicate sufficient reactivity and yet the monomer may be activated for S_NAr as demonstrated by experiment.

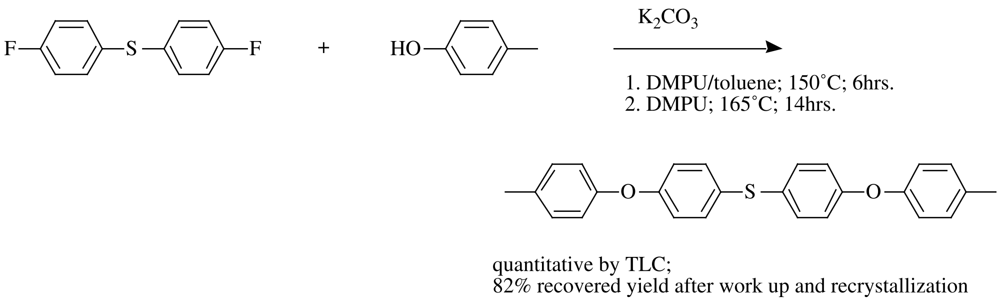
We are interested in investigating other activating groups that may not be obvious choices as strongly electron withdrawing groups, and may not follow the traditional ideas of Meisenheimer complex activation [50,51]. We have found different types of activating groups *para* to a fluoro group to undergo essentially quantitative nucleophilic aromatic substitution with phenoxides by what appears to be a S_NAr mechanism. Continued research will help to elucidate a mechanism, but will focus ultimately on the formation of new materials and their characterization and use. We have investigated two different activation ideas—electron accepting heteroatom activation [51] and ring-opening Meisenheimer stabilization [50].

In investigating S_NAr activation by heteroatoms, two specific examples can be found in the literature. The first is the activation by halogens, most notably, fluorine and chlorine. It is found that hexafluorobenzene readily undergoes substitution by nucleophiles as a result of the electron withdrawing capability of fluorine [66,67]. In this case, a resonance stabilized Meisenheimer complex cannot be drawn and the activation is predominately the result of inductive effects. Perfluoroalkyl groups have also been found to activate substitution by an inductive electron withdrawing effect and have been used as activating groups for polymerization [33].

Another example of activation by halogens can be found in the synthesis of poly(phenylene sulfide), PPS. PPS is a commercial engineering polymer produced by a high temperature condensation reaction. The reaction occurs between *para*-dichlorobenzene and the good nucleophile, sodium sulfide. Detailed mechanistic studies have been performed to demonstrate that the reaction occurs by S_NAr whereby the initial activation for *para* substitution is from the inductive electron withdrawing character of the electronegative chloro group [63,68]. The reaction proceeds quantitatively only at



Scheme 1. Synthesis of bis(4-fluorophenyl)sulfide.



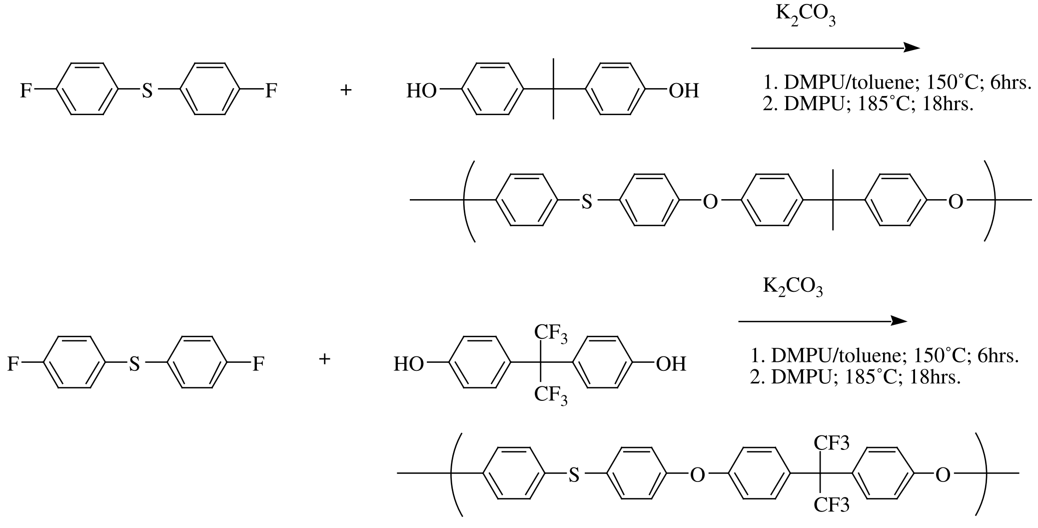
Scheme 2. Synthesis of model compound from bis(4-fluorophenyl)sulfide and *p*-cresol.

temperatures in excess of 200 °C and only with the strongly nucleophilic sulfide or thiophenoxide. The same reaction does not occur for the weaker phenoxide nucleophile to make the corresponding poly(phenylene ether).

What is perhaps unexpected in the PPS reaction, is that an intermediate structure, bis(4-chlorophenyl)sulfide, is more activated toward substitution than the original *para*-dichlorobenzene. In model studies, the bis(4-chlorophenyl)sulfide is 14 times more reactive with sodium sulfide than the *para*-dichlorobenzene indicating the unusual activation by a sulfide group [63]. This is unexpected because the electronegativity of sulfur, unlike chlorine, is comparable to carbon, and sulfur typically acts as an electron donating group by resonance in many other reactions. An attempt to explain the reactivity by correlation analysis of relative reaction rates against Hammet σ_p^- values was done, but found the sulfide group to show an anomalously higher reactivity.

To investigate arylfluoride substitution with phenoxide nucleophiles by sulfide activation, bis(4-fluorophenyl)sulfide was synthesized by a Friedel–Crafts reaction between fluorobenzene and thionyl chloride followed by reduction of the sulfoxide to the sulfide with oxalyl chloride and tetrabutylammonium iodide (Scheme 1) [54].

Model substitution reactions were performed with a small excess of *para*-cresol and the bis(4-fluorophenyl)sulfide using the polar aprotic solvent, DMPU, under conditions that simulate the reaction conditions for typical poly(aryl ether) synthesis (Scheme 2). Quantitative conversion was observed by thin layer chromatography, and the model compound was isolated and purified to demonstrate reaction to the desired



Scheme 3. Polymerization of bis(4-fluorophenyl)sulfide with bisphenol A and bisphenol AF.

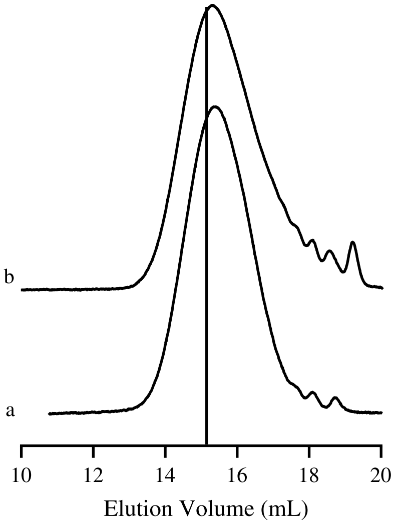


Fig. 1. GPC chromatograms of poly(aryl ether sulfide)s after 18 h at 185 °C. Vertical line is the elution volume for a 16,000 g/mol polystyrene standard; (a) polymer from bisphenol AF M_n 11,600 g/mol, $M_w/M_n = 1.60$; (b) polymer from bisphenol A M_n 8100 g/mol, $M_w/M_n = 2.19$.

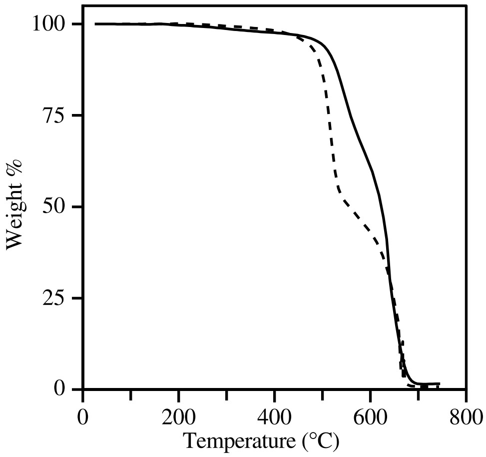


Fig. 2. TGA of poly(aryl ether sulfide)s: – – –bisphenol A; — bisphenol AF.

ether product. The results complement those demonstrated in PPS synthesis; however, the use of bis(4-fluorophenyl)sulfide monomer rather than dichlorobenzene allows ether forming reactions with phenoxide nucleophile to proceed in high yield.

The sulfide-activated monomer was reacted with bisphenols in order to examine the conversion to polymers (Scheme 3). Reaction with bisphenol A or bisphenol AF under similar reaction conditions as for the model compound synthesis resulted in significant molecular weight growth in each case. GPC chromatograms are shown in Fig. 1 to demonstrate the molecular weight distribution and are compared graphically to a 16,000 g/mol polystyrene standard. The chromatograms have the appearance of typical GPC chromatograms for poly(aryl ether)s, depicting a polydispersity that approaches a value of 2 and some low molecular weight cyclic oligomers at high elution volume formed during the polymerization. The extent of arylfluoride conversion calculated from the molecular weights obtained is 98% in each case. Higher molecular weight polymers have thus far not been achieved and the reason is speculated to be due to the difficulty in adequately purifying the liquid bis(4-fluorophenyl)sulfide monomer.

While only moderate molecular weights have thus far been attained for the poly(aryl ether sulfide) polymers, characterization of their thermal properties can be done. The glass transition temperatures and thermogravimetric characterization results, along with molecular weights are reported in Table 1. The thermal stability results (Fig. 2) are comparable to the similar materials obtained by reduction of poly(aryl ether sulfoxide)s [53] and demonstrate the good thermal stability of the materials. Glass transition temperatures are low compared to other poly(aryl ether)s that contain strong polar activating groups. The lack of strong polar groups, however, also makes these materials interestingly different from other poly(aryl ether)s, as low dielectric constants would be expected.

Table 1
Characterization of poly(aryl ether sulfide)s

Bisphenol monomer	M_n[a] (g/mol)	M_w/M_n[a]	T_g[b] (°C)	5% wt. loss[c]
Bisphenol A	8100	2.19	91	463
Bisphenol AF	11,600	1.60	119	491

[a] By GPC relative to polystyrene standards.
[b] From DSC with a heating rate of 10 °C/min.
[c] From TGA with a heating rate of 10 °C/min under an air atmosphere.

Solubility of the poly(aryl sulfide)s were examined and both the polymer from bisphenol A and that from bisphenol AF were found to be quite soluble in a number of common solvents including chloroform, *N*,*N*-dimethylacetamide, toluene, THF, methylene chloride, and DMSO. The polymers are insoluble in methanol, isopropanol, hexanes, and acetonitrile. The polymer from bisphenol AF was found to be slightly soluble in warm acetone, while the polymer from bisphenol A was insoluble. The polymers were solution cast from THF to result in rather brittle films, reflective of the relatively low molecular weights.

Parallel to the study of bis(4-fluorophenyl)sulfide, we have investigated another sulfide activated monomer, 2,7-

Table 2
Characterization of poly(aryl ether thianthrene)s

Bisphenol monomer	M_n[a] (g/mol)	M_w/M_n[a]	T_g[b] (°C)	5% wt. loss[c]	Char yield at 750 °C[c] (%)	Refractive index
Bisphenol A	22,600	2.10	161	484	50.2	1.6705[d], 1.6787[e], 1.7024[f]
Bisphenol AF	34,300	6.21	181	491	56.3	1.6130[d], 1.6205[e], 1.6406[f]

[a] By GPC relative to polystyrene standards.
[b] From DSC with a heating rate of 10 °C/min.
[c] From TGA with a heating rate of 10 °C/min under a helium atmosphere.
[d] At wavelength 656 nm.
[e] At wavelength 589 nm.
[f] At wavelength 486 nm.

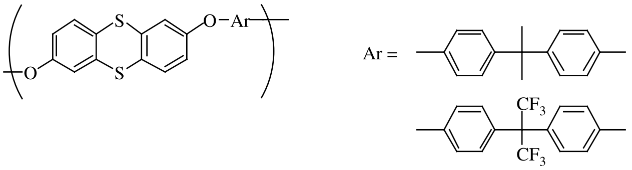


Fig. 3. Poly(aryl ether thianthrene)s.

difluorothianthrene. This monomer is a high melting crystalline solid that sublimes under reduced pressure, compared to the liquid bis(4-fluorophenyl)sulfide, simplifying purification for polymer synthesis. We have recently demonstrated the reactivity of 2,7-difluorothianthrene as an activated monomer for nucleophilic aromatic substitution and have produced high molecular weight poly(aryl ether thianthrenes) under fairly mild reaction conditions [51]. The high molecular weight further demonstrates the general activation by a sulfide group for nucleophilic aromatic substitution. Molecular weight characterization data for the highest molecular weight samples produced from bisphenol A and bisphenol AF are reproduced in Table 2. Since the initial report on the synthesis of the poly(aryl ether thianthrene)s [51], we have further characterized the materials and present the data here.

The poly(aryl ether thianthrene)s (Fig. 3) were examined for some of their optical properties. Because of the high sulfur content, the polymers were expected to have high refractive index values that depend on the bisphenol composition. The wavelength dependent refractive index values are reported in Table 2, and show values as high 1.70 for the bisphenol A polymer at a blue light wavelength.

The poly(aryl ether thianthrene)s were analyzed through a simple flammability test by inserting the solvent cast and thoroughly dried films into a Bunsen burner flame. The polymer samples ignited and burned, but did not show any evidence of dripping while burning. Furthermore, as evidenced by the series of still images from a Quicktime movie, (Fig. 4)

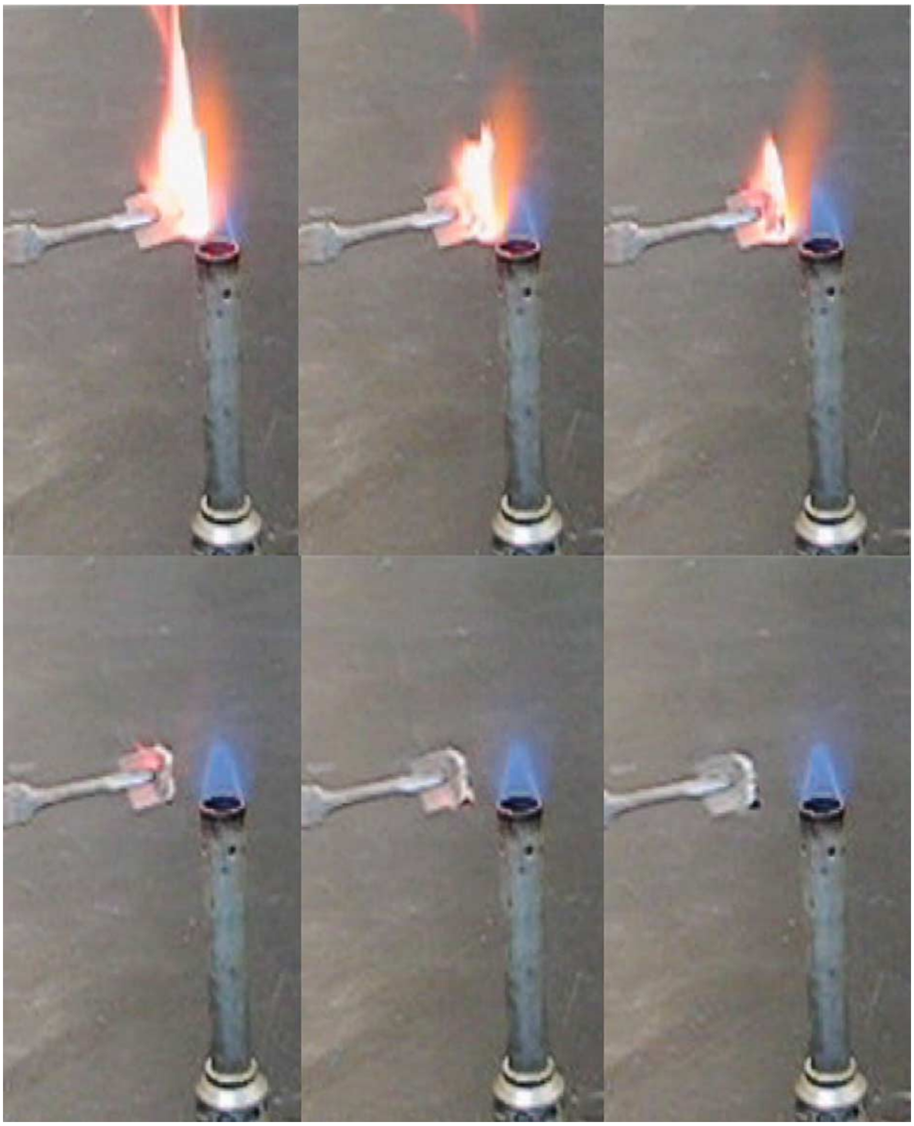


Fig. 4. Series of consecutive Quicktime movie frames from flammability test of poly(aryl ether thianthrene) from bisphenol A.

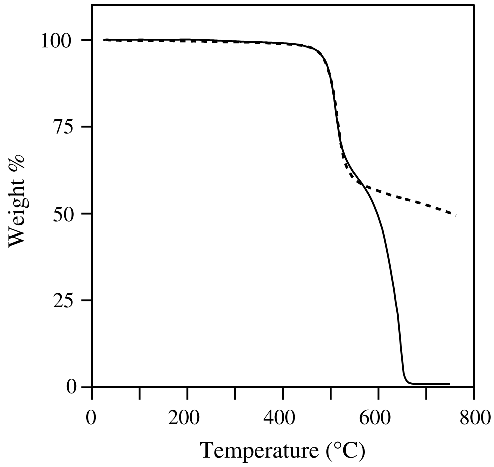


Fig. 5. TGA of poly(aryl ether thianthrene) from bishenol A: – – – helium atmosphere; — air atmosphere.

the material immediately extinguished itself upon removal from the flame. The series of consecutive frames in Fig. 4 depict a time sequence of approximately 0.2 s. The polymer samples showed high char yields during the Bunsen burner test (greater than 30% after 3 min), as previously reported [51], but the TGA in an air atmosphere does not reflect the tendency to produce a non-burning char. TGA under an inert atmosphere (helium in this case) demonstrates the high char yield, as depicted in Fig. 5. The polymer from bisphenol AF shows a similar result (Fig. 6). The results for the TGA in air versus in an inert atmosphere demonstrate the difficulty in adequately screening materials during initial testing of flammability and show that in this case, TGA in an inert atmosphere rather than air is a better predictor of flammability.

4. Conclusions

Aryl sulfides appear to activate aryl fluorides for substitution in nucleophilic aromatic substitution polymerization with phenoxide monomers. Both bis(4-fluorophenyl)sulfide and 2,7-diflorothianthrene have been polymerized with bisphenol monomers to high extents of conversion. The resulting aryl ether sulfide polymers show good thermal stabilities, and moderate glass transition temperatures corresponding to their relatively low polarity. The poly(aryl ether thianthrene)s show exceptional resistance to burning and have high refractive index values making them potentially useful in a variety of applications. Further work will focus on the mechanism of polymerization and continuing to investigate activating groups for nucleophilic aromatic substitution.

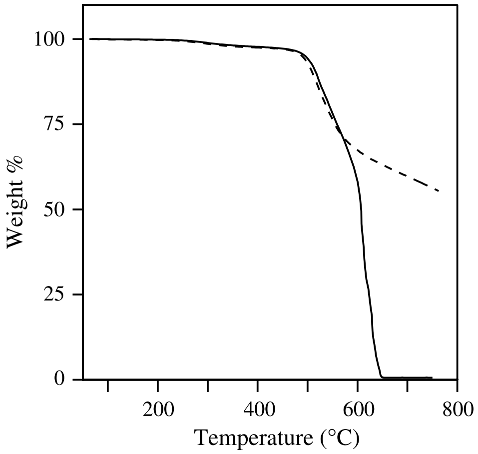


Fig. 6. TGA of poly(aryl ether thianthrene) from bishenol AF: – – – helium atmosphere; — air atmosphere.

Acknowledgements

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