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Communications to the Editor

Thiophene-Based Poly(arylene ether)s. 4. Synthesis of Poly(arylene ether sulfone)s

R. S. Archibald, V. V. Sheares, E. T. Samulski, and J. M. DeSimone*

Venable and Kenan Laboratories, Department of Chemistry, University of North Carolina at Chapel Hill, CB #3290, Chapel Hill, North Carolina 27599-3290

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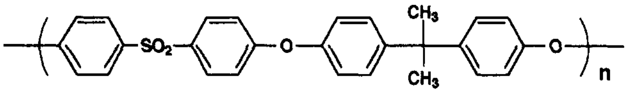
Poly(arylene ether sulfone)s are recognized as important high-performance engineering thermoplastics as they possess excellent strength, oxidative, thermal, and hydrolytic stability, making them useful as ultrafiltration components, composites, coatings, and adhesives.[1,2] Representative commercially available materials include Union Carbide's Udel (1) and ICI's Victrex (2). Early work on poly(arylene ether sulfone)s focused on optimizing the synthetic conditions to achieve high molar mass polymers[3] and developing alternative synthetic routes which tolerate a variety of substituted monomers.[4] Current work seeks to design materials that add to the inherent properties of these polymers, resulting in their extension into a broader variety of applications.[5]



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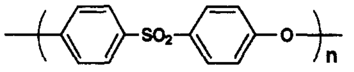

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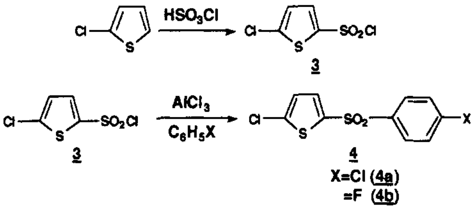
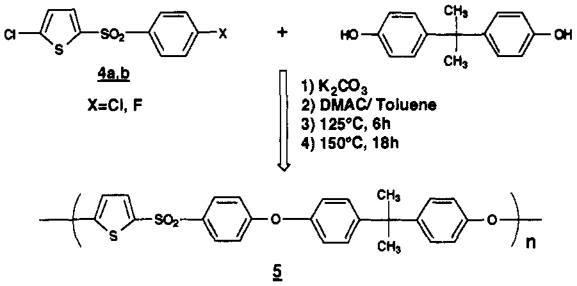
Our approach to macromolecular engineering of properties exploits the development of new, thiophene-based versions of traditionally phenylene-based polymers. Samulski *et al.* began studying thiophene as a structural unit in low molar mass compounds to ascertain the limiting geometries that are compatible with liquid crystal formation.[6] They discovered that mesomorphism is maintained when the nonlinear 2,5-thiophene moiety is substituted for the linear 1,4-phenylene or 4,4'-biphenyl moiety in low molar mass liquid crystals. These initial findings have been extended to several classes of liquid crystalline polymers including thermotropic poly(ester)s[7] and lyotropic poly(benzoxazole)s[8] and poly(aramid)s.[9]

Having demonstrated the viability of the thiophene moiety in liquid crystalline polymers, other classes of high-performance materials became of interest, in particular, poly(arylene ether ketone)s. Within this class of polymers, our initial work described the polymerization of bis(*p*-fluorobenzoyl)thiophene with 4,4'-isopropylidenediphenol.[10] The resulting polymer was of high molar mass and possessed comparable properties to the *p*-phenylene and *m*-phenylene derivatives, clearly demonstrating the stability of thiophene under the polymerization conditions. More recently, we described extensions of this work to the synthesis of explicit thiophene analogues of poly(arylene ether ketone)s. This required the development of a new synthetic methodology employing thienyl–phenyl ether bond formation as the polymer forming step; the methodology was demonstrated in the reaction of bis(5-chlorothienyl-2) ketone and 4,4'-isopropylidenediphenol which resulted in a high molar mass polymer.[11] Subsequently the monoketone system has been adapted to include wholly aromatic diketone monomers.[12] Herein, we report another extension of this new polymerization methodology to the synthesis of thiophene-based poly(arylene ether sulfone)s. It is anticipated that the bilaterally asymmetric heterocycle in the polymer backbone, i.e., the quasi-functionality of the sulfur heteroatom, will affect physical characteristics such as the glass transition temperature (T_g), solubility, miscibility, adhesion, and gas permeability.

Scheme I



Scheme II



In order to begin this investigation of poly(arylene ether sulfone)s, two new activated bis(halide aryl) sulfone monomers, 2-chloro-5-[(4'-chlorophenyl)sulfonyl]thiophene (**4a**) and 2-fluoro-5-[(4'-chlorophenyl)sulfonyl]thiophene (**4b**), were synthesized (Scheme I). The precursor, 2-chloro-5-(chlorosulfonyl)thiophene (**3**),[13] was synthesized by treating chlorothiophene with chlorosulfonic acid in chloroform at low temperature. The optimum route for forming the sulfone monomers (**4a,b**) involved the stoichiometric Friedel–Crafts sulfonylation of **3** with aluminum chloride in the halobenzene. The sulfone monomers **4a**[14] and **4b**[15] were formed in quantitative yield and easily purified by recrystallization in methanol. The resulting monomers were greater than 99.9% pure by gas chromatography.[16]

Polymer synthesis (Scheme II) was conducted in a three-necked 100-mL round-bottomed flask equipped with an overhead stirrer, a Dean–Stark trap, a condensor, a gas inlet, and a thermometer. The flask was charged with **4a** (0.01364 mol), Bisphenol A (0.01364 mol), dimethylacetamide (35 mL), potassium carbonate (0.04 mol, 3 equiv), and toluene (4 mL). This solution was heated between 120 and 125 °C whereby dehydration occurred via con-

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* Author to whom correspondence should be addressed.

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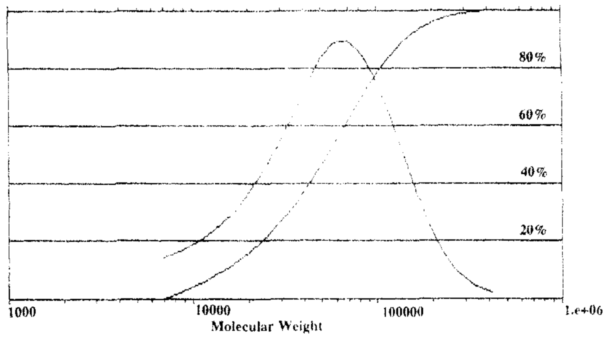

Figure 1. GPC-calculated molar mass distribution for the thiophene-based poly(arylene ether sulfone) (**5**) fractionally precipitated from methylene chloride with methanol.

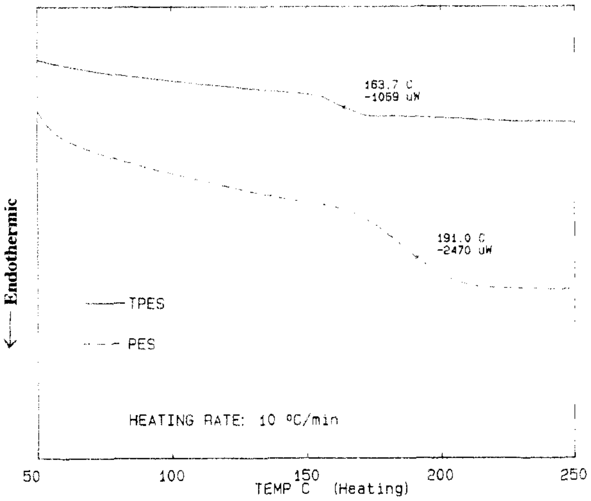

Figure 2. Differential scanning calorimetry (DSC) thermograms of the phenyl analog (PES) and thiophene-based poly(arylene ether sulfone) (TPES).

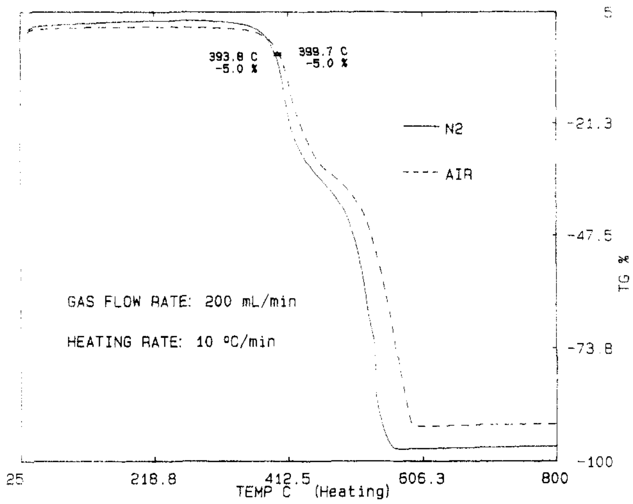

Figure 3. Thermal gravimetric analysis (TGA) thermograms of the thiophene-based poly(arylene ether sulfone) in air and nitrogen.

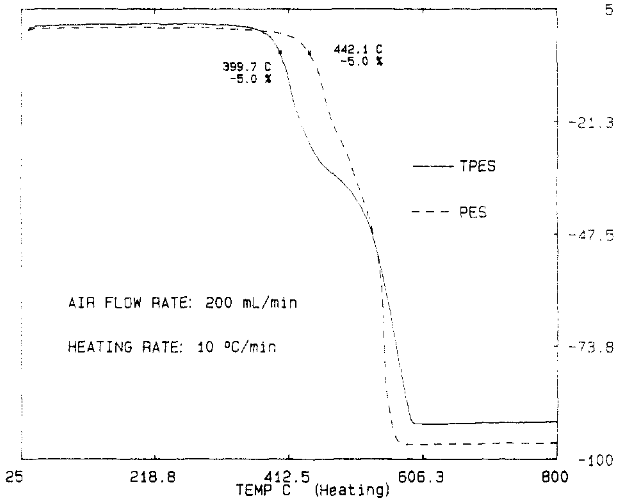

Figure 4. Thermal gravimetric analysis (TGA) thermograms of the thiophene-based poly(arylene ether sulfone) (TPES) and its phenyl analog (PES) in air.

tinual removal and addition of toluene (25 mL) over 6 h. After dehydration, the solution was heated at 150 °C for 18 h to obtain complete polymerization. The polymer was coagulated into a 50/50 water/methanol solution, dried, and reprecipitated from methylene chloride into methanol.

These resulting poly(arylene ether sulfone)s (**5**) were of high molecular weight as determined by GPC[17] (Figure 1); the polymer from the fluorine-based monomer (**4b**) yielded the highest molar mass. We attribute this molecular weight difference to greater reactivity of the fluorine-based monomer versus the chlorine-based monomer in nucleophilic substitution reactions. ^{1}H NMR analysis showed easily distinquishable thiophene, phenyl, and methyl protons.[18] One key resonance at δ 6.4 is characteristic of the thiophene proton ortho to the ether linkage. The regiochemistry resulting from these asymmetric monomers is clearly observed by ^{1}H NMR and will be fully elaborated in a future publication.[23] A solvent-cast, vacuum-dried film of the polymer was transparent, tough, and amber in color. The new polymer has a T_g = 164 °C (approximately 30 °C lower than the all-phenyl-based analogue; Figure 2).[19] Thermogravimetric analysis (TGA)[20] of polymer **5** in both air and nitrogen showed 5% weight loss at 400 and 394 °C, respectively (Figure 3). In air, the thiophene-based poly(arylene ether sulfone) decomposes (as determined by TGA) approximately 40 °C lower then the all-phenyl analog (Figure 4).[21]

In conclusion, it is apparent that nucleophilic displacement of activated bishalothiophenes with bisphenates leads to high molar mass, thiophene-based poly(arylene ether sulfone)s, indicating the quantitative nature of the substitution chemistry utilized. Aromatic nucleophilic displacement chemistry on heterocycles appears to be a promising and general synthetic route to new classes of poly(arylene ether)s; this chemistry was also recently demonstrated by Maier and co-workers for the synthesis of poly(arylene ether oxazole)s.[22] The thiophene-based materials described herein use facile synthetic routes and economically feasible starting materials, and this new methodology opens the way to a large variety of heterocyclic and aromatic poly(arylene ether sulfone)s. Moreover, this chemistry should prove important for the synthesis of polymeric materials for chelation chemistry, adhesion investigations, and design strategies for controlled structures in a variety of applications such as permselective membranes.

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Supplementary Material Available: Listings of detailed experimental syntheses of **3**, **4a**, and **4b** (2 pages). Ordering information is given on any current masthead page.

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(13) 50% yield of a colorless oil, bp = 76–80 °C at 0.1 Torr. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.67 (d, 1H, J = 4.1 Hz, proton ortho to chlorine atom), 7.03 (d, 1H, J = 4.1 Hz, proton ortho to sulfonyl chloride group). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 142.12 (carbon attached to sulfonyl chloride), 141.26 (carbon attached to the chlorine atom), 134.52 (carbon ortho to chlorine atom), 127.52 (carbon ortho to sulfonyl chloride).

(14) White crystals, T_m = 99.6 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.82 (d, 2H, J = 8.73 Hz, phenyl proton ortho to the sulfone group), 7.43 (d, 2H, J = 8.73 Hz, phenyl proton ortho to the chlorine atom), 7.42 (d, 1H, J = 4.13 Hz, thiophene proton ortho to the sulfone group), 6.86 (d, 1H, J = 4.13 Hz, thiophene proton ortho to the chlorine atom). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.35, 140.02, 139.90, 133.07 (thiophene carbon ortho to the sulfone group), 129.82 (phenyl carbon ortho to the chlorine atom), 128.82 (phenyl carbon ortho to the sulfone group), 128.61, 127.43 (thiophene carbon ortho to the chlorine atom).

(15) White crystals, T_m = 89.9 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.95 (dd, 2H, $^3J_{HH}$ = 8.82 Hz, $^4J_{HF}$ = 4.9 Hz, phenyl proton ortho to the sulfone group), 7.47 (d, 1H, J = 3.92 Hz, thiophene proton ortho to the sulfone group), 7.19 (dd, 2H, $^3J_{HH}$ = 8.82 Hz, $^3J_{HF}$ = 8.56 Hz, phenyl proton ortho to the fluorine atom), 6.90 (d, 1H, J = 3.92 Hz, thiophene proton ortho to the chlorine atom). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.61 (d, $^1J_{CF}$ = 256.8 Hz, carbon with fluorine substitution), 140.69, 139.56, 137.59, 132.92 (thiophene carbon ortho to the sulfone group), 130.26 (d, $^3J_{CF}$ = 9.6 Hz, phenyl carbon ortho to the sulfone group), 127.46 (thiophene carbon ortho to the chlorine atom), 116.83 (phenyl carbon ortho to the fluorine atom).

(16) A Hewlett-Packard gas chromatograph (5890 Series II) and gas chromatograph mass spectrometer (5890A-5971A) were used for product identification.

(17) Gel permeation chromatography of polymers **5** possessed molecular weights of $M_n = 1.9 \times 10^4$, M_w/M_n = 2.3 (from **4a**) and $M_n = 2.5 \times 10^4$, M_w/M_n = 2.2 (from **4b**) relative to polystyrene standards. The polymers were fractionally precipitated (3×) from methylene chloride into methanol. Gel permeation chromatography of these polymers **5** possessed molecular weights of $M_n = 2.4 \times 10^4$ (from **4a**) and $M_n = 3.5 \times 10^4$ (from **4b**) relative to polystyrene standards. Molar mass and molar mass distributions were examined using a Waters 150-CV gel permeation chromatograph with Ultrastyragel columns of 100-, 500-, 10^3-, 10^4-, and 10^5-Å porosities in tetrahydrofuran with polystyrene standards (Showa Denko).

(18) Proton and carbon NMR studies were completed in $CDCl_3$ on a Varian XL-400 NMR spectrometer. When possible, chemical shift assignments were made using either or both HETCOR and COSY 2-D NMR programs.

(19) Melting points and glass transition temperatures were determined using a Seiko 220 (C) differential scanning calorimeter.

(20) Thermogravimetric analyses were performed on a Seiko 220 RTG at a scan rate of 20 °C/min from 25 to 1200 °C in nitrogen and air.

(21) The all-phenyl-based sulfone polymer (1) was synthesized in the same manner as **5** except that bis(4-chlorophenyl) sulfone was substituted for **4**.

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