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THIOPHENE BASED POLY(ARYLENE ETHER SULFONE)S: POLYMERIZATION OF 2-CHLORO-5-(4'-HALOPHENYL-SULFONYL) THIOPHENE WITH 4,4'-ISOPROPYLIDENEDIPHENOL

BY

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13. ABSTRACT (Maximum 200 words) Poly(arylene ether sulfone)s (PAES) are recognized as important high performance engineering thermoplastics. ^{1,2} These commercially available materials are commonly represented by Union Carbide's Udel TM (1) and Cl's Victrex TM (2). These PAES materials possess excellent strength, oxidative, thermal, and hydrolytic stability and are useful for ultrafiltration components, composites, coatings, and adhesives.				
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Thiophene Based Poly(arylene ether sulfone)s: Polymerization of 2-Chloro-5-(4'-halophenylsulfonyl)thiophene with 4,4'-Isopropylidenediphenol

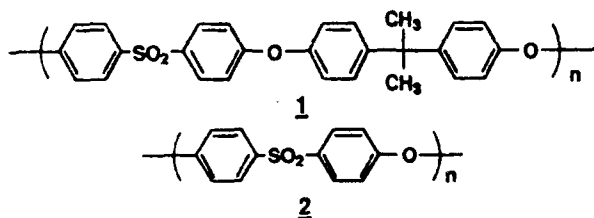
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Introduction.

Poly(arylene ether sulfone)s (PAES) are recognized as important high performance engineering thermoplastics.^{1,2} These commercially available materials are commonly represented by Union Carbide's Udel™ (1) and Cl's Victrex™ (2). These PAES materials possess excellent strength, oxidative, thermal, and hydrolytic stability and are useful for ultrafiltration components, composites, coatings, and adhesives.



Johnson and Farnham³ showed that poly(arylene ether sulfone)s could be made through the step growth polymerization of 4,4'-dichlorodiphenylsulfone and various bisphenols using aprotic solvents such as dimethylsulfoxide (DMSO) and potassium hydroxide. McGrath⁴ found that this polymerization proceeded with excess potassium carbonate and dimethylacetamide as a solvent eventually resulting in the polymerization of new sulfone monomers.⁵

DeSimone and Samulski have introduced thiophene into the backbone of polymeric analogs of the commercially known poly(ethylene terephthalate)⁶, poly(ether ether ketone)s⁷, poly(benzoxazole)s⁸ and poly(aramid)s such as DuPont's Kevlar™.⁹ Thiophene's introduction into these materials was readily achieved using conventional polymerization techniques and does not disrupt many of the favorable properties such as thermal stability, liquid crystallinity, strength and other mechanical properties. The presence of a heteroatom in the thiophene is expected to affect its membrane permeability, polymer blending, and adhesive properties when introduced into poly(arylene ether sulfone)s. Herein we report the extension of these developments to the synthesis of thiophene-based poly(arylene ether sulfone)s.

Experimental.

Monomer Synthesis

2-Chloro-5-(sulfonylchloro)thiophene (3). A 2000 mL beaker was charged with a magnetic stirrer, chlorosulfonic acid (1.72 moles), CHCl_3 (100 mL), and dry ice to maintain the temperature between 0 and -10°C . Chlorothiophene (0.84 moles) was added dropwise over ten minutes which

turned the mixture dark black. The solution was allowed to warm to room temperature and then was cooled to -10°C with the addition of dry ice. The excess chlorosulfonic acid was quenched with water ice and the organic layer was separated from the aqueous layer. The aqueous layer was extracted with methylene chloride and the organic layers were combined, dried over MgSO_4 , filtered and concentrated *in vacuo*. Vacuum distillation (0.1 torr, $76-80^\circ\text{C}$) of the isolated oil yielded 93g (50%).

2-Chloro-5-(4'-chlorophenylsulfonyl)thiophene (4a). General monomer synthesis conditions. A 300 mL three necked round bottom flask, topped with a reflux condenser, was charged with (3) (0.14 moles) chlorobenzene (1.3 moles), and aluminum chloride (0.14 moles). The black reaction mixture was stirred for two hours. The reaction was complete at this time by GC analysis. The reaction was quenched with water and the organic and aqueous layers were separated. The aqueous layer was further extracted with methylene chloride and the organic layers were combined. The organic layers were dried over MgSO_4 , filtered, and concentrated *in vacuo* leaving a solid in quantitative yield. The solid was recrystallized in methanol (3x) using carbon black initially to decolorize the hot methanol solution. Both compounds gave white crystals **4a** $T_m = 108.8^\circ\text{C}$ and **4b** $T_m = 99.9^\circ\text{C}$.

General Polymer Synthesis

Synthesis was conducted in a three necked 100 mL round bottom flask equipped with an overhead stirrer, a Dean-Stark trap, condenser, gas inlet and thermometer. The flask was charged with **4a** (0.01364 moles) bisphenol A (0.01364 moles), dimethylacetamide (35 mL), potassium carbonate (0.04 moles, 3 eq.) and toluene (4 mL). This solution was heated between $120-125^\circ\text{C}$ whereby dehydration occurred via subsequent removal and addition of toluene over 6 h. After dehydration, the solution was heated at 150°C for 18 h to obtain complete polymerization. The polymer was coagulated in a 50/50 water/methanol solution, dried, and reprecipitated from methylene chloride into methanol. The polymers were fractionally precipitated (3X) from tetrahydrofuran with water. Gel permeation chromatography of polymers **5** possessed molecular weights of $M_n = 25000$ (from **4a**) and $M_n = 35000$ (from **4b**) relative to poly(styrene) standards.

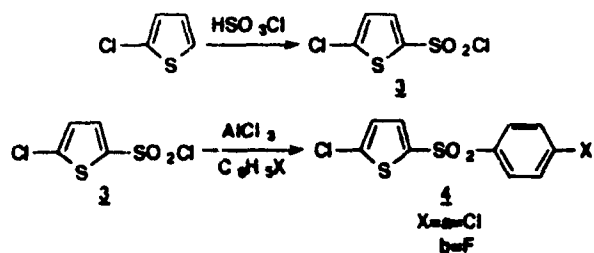
Characterization

Proton and Carbon NMR studies were completed in CDCl_3 on a Varian XL-400 400 MHz NMR spectrometer. A Hewlett-Packard Gas Chromatograph (5890 Series II) and Gas Chromatograph Mass Spectrometer (5890A-5971A) were used for product identification. Melting points and glass transition temperatures were determined using a Perkin-Elmer DSC-7. Molar mass and molar mass distributions were examined using a Waters 150-CV gel permeation chromatograph with Ultrastaygel columns of 100, 500, 10^3 , 10^4 , and 10^5 Å porosities in tetrahydrofuran was used with poly(styrene) standards (Showa Denko).

Results and Discussion.

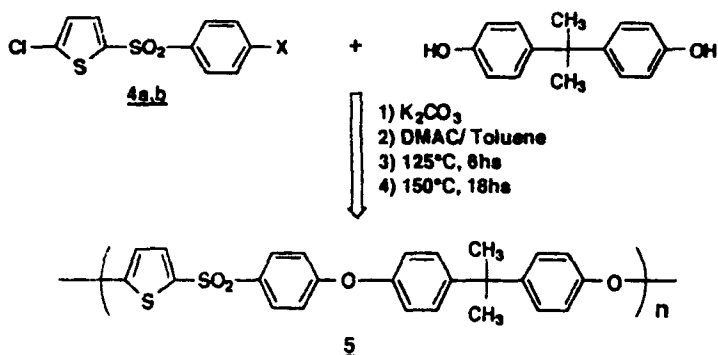
The optimum route for forming the sulfone monomers (**4a,b**) involved the stoichiometric Freidel Crafts sulfonylation of **3**; the sulfonyl chloride of chlorothiophene. The sulfone monomers were formed in quantitative yield (Scheme 1) and easily purified by recrystallization in methanol. The resulting monomers were greater than 99.9% pure by GC.

Scheme I



The polymerizations (Scheme II) were performed with a stoichiometric ratio of monomers, 50% excess of potassium carbonate in dimethylacetamide. This resulting polymers **5** were of high molecular weight as determined by GPC data with the polymer from monomer **4b** yielded the highest molar mass. We attribute this molecular weight difference to the greater reactivity of the fluorine-based monomer versus the chlorine-based monomer to nucleophilic substitution. A solvent cast, vacuum-dried film of the polymer was of high quality and strength. This film is transparent, amber colored, and very creasable with a $T_g = 160^\circ\text{C}$ (approximately 30°C lower than Udel).

Scheme II



Conclusions

Freidel Crafts sulfonation was used to synthesize thiophene based sulfone monomers. Polymerization of these monomers led to high molecular thiophene based poly(arylene ether sulfone)s. These thiophene containing polymers show similar properties to the phenyl-based poly(arylene ether sulfone)s. Detailed thermal analysis of these new materials will be presented at the meeting.

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