

SULFONATED POLY(ARYLENE ETHER SULFONE) AS CANDIDATES FOR PROTON EXCHANGE MEMBRANES: INFLUENCE OF SUBSTITUTION POSITION ON MEMBRANE PROPERTIES

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Introduction

Poly (arylene ethers) are well known engineering thermoplastics with many desirable properties.¹ Among these are good mechanical strength, high thermal and thermo-oxidative stabilities, especially when devoid of aliphatic groups. Sulfonated poly (arylene ether sulfone) have been investigated by many research groups, but primarily produced via post-polymerization sulfonation (i.e., chlorosulfonic acid, sulfuric acid, fuming sulfonic acid). The resulting pendant sulfonic acid is placed almost exclusively on the activated bisphenol moiety.² Our research group has alternatively produced disulfonated poly (arylene ether sulfone) copolymers via direct copolymerization of sulfonated monomers.³ This approach affords two pendant sulfonate group on the deactivated sulfone unit. This presentation will compare various important properties of the post-sulfonated and the directly copolymerized membranes as they related to hydrogen-air and direct methanol (DMFC) fuel cells. The presentation will emphasize that very different membrane results from the two distinct approaches.

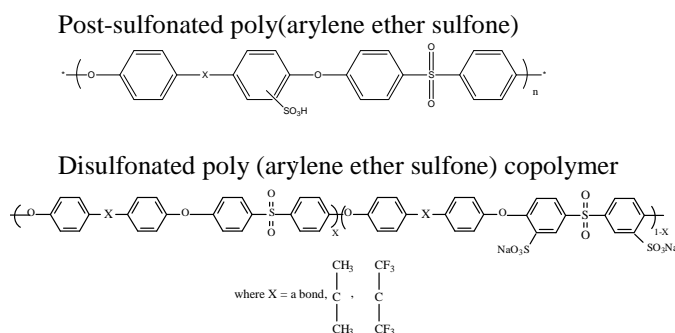


Figure 1. Repeat unit of sulfonated polymers.

Experimental

The synthesis of the disodium salt of dichlorodiphenyl sulfone (SDCDPS) was reported previously.⁴ The post-sulfonated poly arylene ether sulfones were prepared using similar conditions reported by Nolte, et al.⁵ The degree of sulfonation was varied by varying the amount (moles) of chlorosulfonic acid added per gram of polymer, which was pre-dissolved in the dichloroethane solvent.

The direct synthesis of a disulfonated poly(arylene ether sulfone) copolymer with 40 mol % disulfonation is discussed. DCDPS (3.3 mmol), SDCDPS (2.2 mmol), and biphenol (5 mmol) were introduced to a 100-mL, three neck flask equipped with a mechanical stirrer, Dean-Stark trap, condenser, and a nitrogen inlet/outlet. Potassium carbonate (1 g) and 20 mL of NMP were added to the reaction flask to afford ~25% (w/v) solid concentration. Toluene (8 mL) was added to the flask as an azeotropic agent. After refluxing toluene to

dehydrate the reaction mixture for 4 h, the reaction was heated to 190 °C for up to 30 h which resulted in a viscous solution. The solution was diluted with DMAc, cooled to room temperature, and precipitated into an excess of deionized water yielding fibrous copolymers. The sulfonated copolymers were dried under vacuum at 120 °C overnight then at 180 °C for at least 6 hours.

All sulfonated membranes were prepared by dissolving the copolymers in N,N-dimethylacetamide, filtering, and then casting the solution directly onto clean glass plates. All of the copolymer membranes were converted to the sulfonic acid form using dilute sulfuric acid.

Results and Discussion

Post-sulfonated poly (arylene ether sulfone) with varying degree of sulfonation was prepared by changing the amount of chlorosulfonic acid to polymer. The exact degree of sulfonation was difficult to control. Reported discretions in the control and reproducibility of post-sulfonated materials can readily be noted from the literature. The sulfonated copolymers were prepared by direct copolymerization (Figure 1). Comparatively, the degree of disulfonation was easily controlled by varying the ratio of SDCDPS to DCDPS in the copolymerization. All the sulfonated polymer and copolymers were analyzed by ¹H and 2D NMR, infrared spectroscopy, thermogravimetric analysis (TGA), and titration.

Proton NMR was used to identify the molecular structure of the sulfonated copolymers and evaluate the degree of sulfonation. Two dimensional (2D) NMR investigation confirmed the location of the pendant sulfonic acid groups on the post-sulfonated polymers to be almost exclusively on the bisphenol residue, except at very high chlorosulfonic acid to polymer ratio. However, at these high degrees of sulfonation the polymer became almost water soluble (or the water sorption diminished the mechanical properties). Measured thin-film proton conductivities results showed that the direct copolymers have higher conductivities than the post-sulfonated polymers even though the post-sulfonated polymers had high water uptakes at comparable ion exchange capacities (IEC). Fuel cell performance data will be presented for sulfonated (co)polymers with comparable ion exchange capacities.

Conclusions The direct copolymers show greatly enhanced properties and performance relative to the post sulfonated membranes.

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