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Synthesis of Highly Sulfonated Poly(arylene ether sulfone) Random (Statistical) Copolymers Via Direct Polymerization

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SUMMARY: Novel biphenol-based wholly aromatic poly (arylene ether sulfones) containing pendant sulfonate groups were prepared by direct aromatic nucleophilic substitution polycondensation of disodium 3,3'-disulfonate-4,4'-dichlorodiphenyl sulfone (SDCDPS), 4,4'-dichlorodiphenylsulfone (DCDPS) and biphenol. Copolymerization proceeded quantitatively to high molecular weight in N-methyl-2-pyrrolidinone at 190°C in the presence of anhydrous potassium carbonate. Tough membranes were successfully cast from the control and the copolymers, which had a SDCDPS/DCDPS mole ratio of either 40:60 or 60:40 using N,N-dimethylactamide; the 100% SDCDPS homopolymer was water soluble. Short-term aging (30 min) indicates that the desired acid form membranes are stable to 220°C in air and conductivity values at 25°C of 0.110 (40%) and 0.170 S/cm (60%) were measured, which are comparable to or higher than the state-of-the art fluorinated copolymer Nafion 1135 control. The new copolymers, which contain ion conductivity sites on deactivated rings, are candidates as new polymeric electrolyte materials for proton exchange membrane (PEM) fuel cells. Further research comparing their membrane behavior to post-sulfonated systems is in progress.

Keywords: direct random polymerization, sulfonated poly(arylene ether sulfones), proton exchange membranes (PEM), conductivity

Introduction

Sulfonated poly (arylene ether sulfone)s made from polymer post reactions have been of interest since the pioneering work of Noshay and Robeson, who were able to develop a mild sulfonation procedure for the commercially available bisphenol-A based poly(ether sulfone).[1] This approach found considerable interest in the area of desalinization membranes for reverse osmosis and related water purification areas.[2,3] In the post sulfonation reaction, the sulfonic acid group is restricted to the activated position ortho to the aromatic ether bond, as indicated in Structure 1. For the case of the bisphenol A based systems, no more than one sulfonic acid

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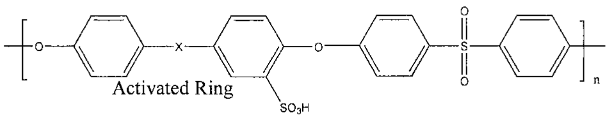
group per repeat unit could be achieved. It was of interest to investigate sulfonation on the deactivated portion of the repeat unit (Structure 2), since one might expect enhanced stability and, perhaps, modestly higher acidity. Indeed, the first report of the required monomer was from Robeson and Matzner[4], who obtained a composition of matter patent, which primarily was of interest for its flame retarding additive properties. More recently, Ueda[5] reported the sulfonation of 4,4'-dichlorodiphenylsulfone and provided general procedures for its purification and characterization -- although details were somewhat limited and no reference to potential applications was indicated. We have modified this procedure somewhat, as described in this paper, and have utilized the material to produce wholly aromatic, film forming, highly sulfonated poly(arylene ether sulfone) copolymer via direct polymerization.



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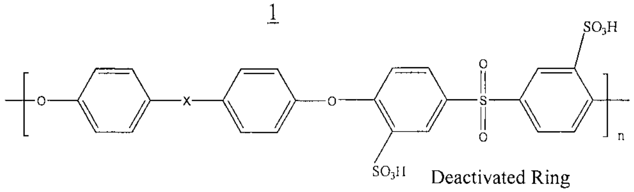

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Our current interest is in the potential of such materials to provide improved and economical proton exchange membranes (PEM) for fuel cell applications.[6-8] The potential for fuel cells based on proton exchange membranes is very substantial, and transport mechanisms have been successfully modeled. [9]

Although the currently important material for PEMs are the statistical copolymers of tetrafluoroethylene and a fluorinated vinyl sulfonic acid, they are known to have some significant technical limitations. These include low modulus at temperatures greater than 80°C, as well as high methanol permeability, which renders sub-optimal the application of these membrane materials in direct methanol fuel cells. The fluoropolymers are also rather expensive, which is considered to be a limiting factor as well. The poly(arylene ether sulfone)s, particularly when devoid of aliphatic units, have excellent thermal and mechanical properties, as well as resistance to oxidation and acid catalyzed hydrolysis.[10,11] This paper describes the synthesis and characterization of a sulfonated high molecular weight poly(arylene ether sulfone) of controlled hydrophilicity. Current efforts are ongoing for its membrane electrode assembly (MEA) and fuel cell evaluation.[12] High performance sulfonated polyimides[13] are also of great interest, including some effort from our laboratory.[14] In addition to the polysulfones, we are actively pursuing somewhat related poly(arylene ether)s containing the diphenyl phenyl phosphine oxide unit [15] and sulfonated poly (phenylene sulfide sulfone)s.[16]

Experimental Section

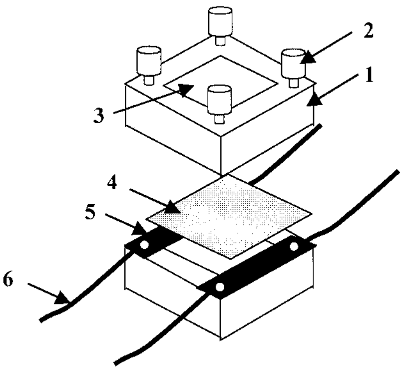
a. Materials: Highly purified, commercially available, 4,4'- dichlorodiphenylsulfone and 4,4'-biphenol were obtained from BP Amoco and Eastman Chemical, respectively. The reaction solvent N-methyl-2-pyrrolidinone (NMP) was distilled from calcium hydride under vacuum before use. All the other reagents were obtained from Aldrich and used as received.

b. Synthesis of the 3,3'-disulfonated 4,4'-dichlorodiphenyl sulfone (SDCDPS): SDCDPS was synthesized by sulfonating dichloro diphenyl sulfone (DCDPS) using fuming sulfuric acid (30%) at 110°C for 6 hours. The resulting acidic compound was neutralized first by sodium chloride and subsequently at room temperature with sodium hydroxide. The monomer grade sulfonated monomer was generated by recrystallization from a mixture of methanol and deionized water. Elemental analysis (assuming a dihydrate) was in good agreement with theory, as was mass spectroscopy and NMR analyses.[17]

c. Synthesis of sulfonated poly(arylene ether sulfone): A typical polymerization for a 60/40 SDCDPS/DCDPS system is described as follows: 1.8621g (10mmol) 4,4'-biphenol, 1.1487g (4mmol) DCDPS, and 2.9476g (6mmol) SDCDPS were added to a simple 3-neck flask equipped with mechanical stirrer, nitrogen inlet and a Dean Stark trap, followed by 1.15 equivalent of potassium carbonate. Dry NMP was introduced to afford a 20% solids concentration and toluene was used an azeotropic agent. The reaction mixture was heated under reflux at 160°C for 4 hours, which stripped off most of the toluene to dehydrate the system. Finally, the temperature was raised slowly to 190°C for 16 hours. The solution became very viscous after this time and was cooled to room temperature and diluted with N,N-dimethyl acetamide, a lower boiling solvent (DMAC). It was filtered to remove most of the salt, and isolated by addition to stirred deionized water. The precipitated fibrous copolymer was washed with hot (80°C) deionized water several times to remove salts and finally vacuum dried at 120°C for 24 hours. Copolymers with other compositions could also be prepared by this procedure and this will be reported later.

d. Membrane preparation: Films were prepared by redissolving the copolymer in DMAC and casting directly onto glass substrates. They were carefully dried by infrared heat at increasing temperatures in a nitrogen atmosphere, then vacuum-dried at 120°C for one day and 150°C for one day. Then the membrane was converted into the acid form with 2 *N* H_2SO_4 for 24 hours. Finally the membrane was washed with de-ionized water and vacuum-dried at 80°C for one day.

e. Characterization: FTIR spectra were recorded using a Nicolet Impact 400 FT-IR spectrometer with homogeneous cast films. NMR spectroscopy was conducted using a Varian 400 megahertz instrument. Intrinsic viscosities were determined at NMP at 25°C using an Ubbelohde viscometer. Non-Aqueous Potentiometric Titrations were conducted using a MCI Automatic Titrator Model GT-05. Conductivity measurements were performed on membranes using the cell shown in Figure 1.



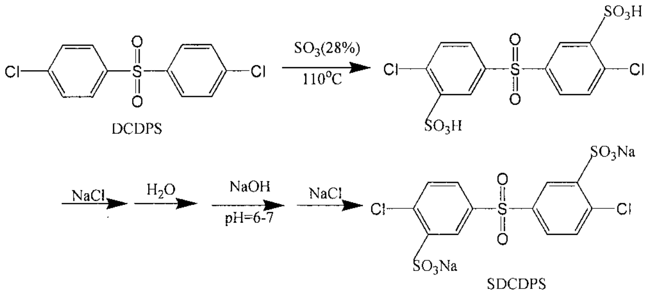
Legend
1. Teflon block
2. Thumbscrew
3. Open area to allow equilibration with environment
4. Membrane sample
5. Blackened Pt foil electrode
6. Pt lead

Figure 1. Conductivity Cell.

This cell geometry was chosen to ensure that the membrane resistance dominated the response of the system. An impedance spectrum was recorded from 10MHz to 10Hz using a Solatron 1260 Impedance/Gain-Phase Analyzer. The resistance of the film was taken at the frequency which produced the minimum imaginary response. All impedance measurements were performed at room temperature under full hydration conditions.

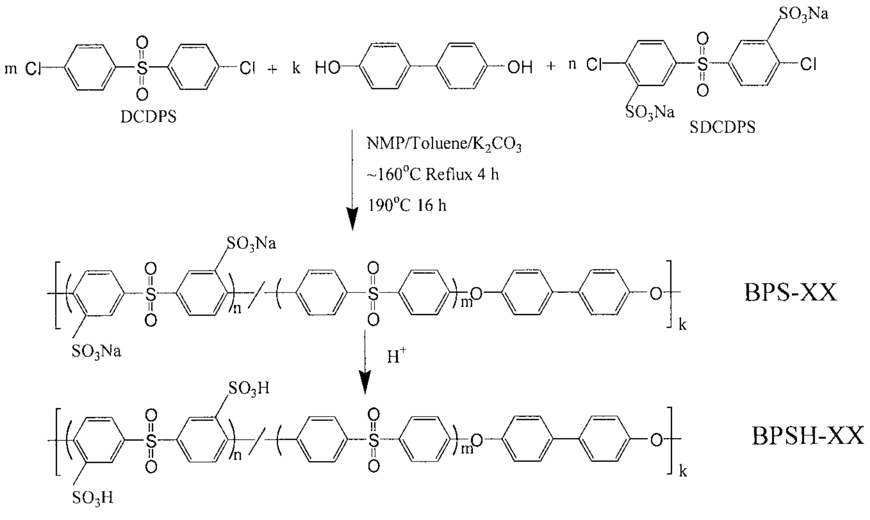
Results and Discussion

The desired sulfonated monomer was prepared as shown briefly in Scheme 1. The 4,4'-dichlorodiphenylsulfone was reacted with fuming sulfuric acid, followed by neutralization with sodium chloride and sodium hydroxide. This electrophilic aromatic substitution process provides derivatives that are meta to the sulfonyl group and ortho to the chlorine group. The chemical structure was confirmed by proton and carbon NMR, as well as by mass spectroscopy, infrared spectra and elemental analysis.[17] The anticipated structures were obtained in yields approaching 80%.



Scheme 1. Synthesis of SDCDPS

Sulfonated poly (arylene ether sulfones) were successfully synthesized via nucleophilic aromatic substitution polycondensation of biphenol, DCDPS and SDCDPS, at 0, 40, 60 and 100% of the SDCDPS. The polymer synthesis (Scheme 2) involved condensing a controlled amount of the sulfonated activated halide, the 4,4'- dichlorodiphenylsulfone and biphenol in NMP, which contained toluene as an azeotropic agent.



(n+m)/k = 1.01 (in mole); XX = 100n/(n+m)

Scheme 2. Synthesis of sulfonated poly(arylene ether sulfones)

The substituted activated halide is clearly less reactive and likely less soluble. Thus, temperatures needed for high molecular weight were increased somewhat higher than normal - to about 190°C. The polymerizations were conducted in the sodium salt form of SDCDPS to take advantage of the greatly enhanced stability of the sulfonic acid salt. However, since potassium carbonate was the base, some alkali sulfonate exchange probably occurred.

Table 1. Synthesis and Characterization of Biphenol Based Sulfonated Copolymer Compositions

25°C	**Monomers (mmol)**		$[\eta]^{NMP}$	**Water Content**	**Conductivity(c)**
Polymer	**DCDPS**	**SDCDPS**	**(dl/g)**	**(%)**$^{(a)}$	**S/cm**
BPS-00	10	0	0.61	0.4	0
BPSH-40	6	4	2.3	31	0.11
BPSH-60	4	6	3.3	78	0.17
BPS-100	0	10	---	WS$^{(b)}$	---

(a): 24 hr at 25°C; (b): Water soluble; (c) Nafion 1135 control was 0.12

The recovered yields were quantitative and intrinsic viscosities determined in NMP at 25°C were high (Table 1). Of course, the intrinsic viscosities are influenced by the sulfonated groups, which is no doubt related to enhanced intermolecular associations. At this point, up to 1.2 $-SO_3Na$ groups per repeating unit (60 mole% SDCDPS) introduced into the polymer chain allowed high molecular weight, tough, film-forming material to be obtained. In addition, all the sulfonated membranes show higher water uptake than non-sulfonated membrane, due to the introduction of hydrophilic sulfonate groups. (Table 1.) The 100% SDCDPS system was water soluble. Sodium form membranes (BPS) were transferred to corresponding acid form (BPSH) using dilute acid solution for characterization and conductivity measurements.

The successful introduction of the sodium sulfonate groups was confirmed by the FT-IR spectra of BPS, (Figure 2a, 2b) where strong characteristic peaks at 1030 cm^{-1} and 1098 cm^{-1} were assigned to symmetric and asymmetric stretchings of SO_3Na. [18] As shown in 1c, there is no related mode for the unsubstituted control material prepared from biphenol and DCDPS. One can compare these three, as well as by the NMR methods reported by Johnson et al.[2]

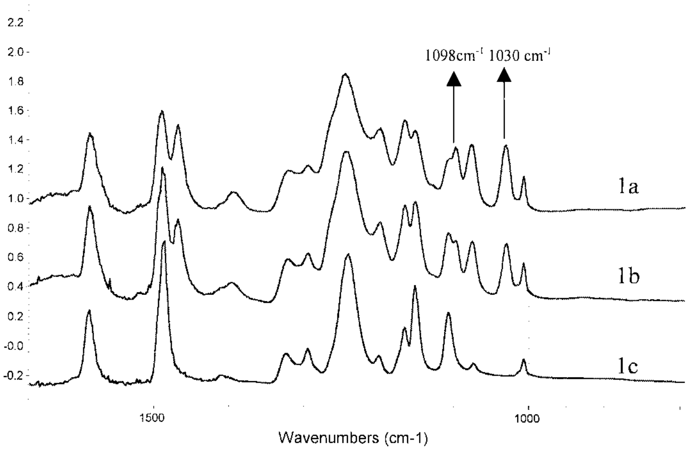


Figure 2. IR Spectra of (1a) 60% and (1b) 40% sulfonated polymer and (1c) Non-substituted polymer control.

Table 2. Short-term thermal stability of -SO_3H groups of 40 or 60 mole % copolymers as Indicated by Intrinsic Viscosity and IEC Retention at 25°C(a)

Aging T,	BPSH-40		BPSH-60	
°C	IV[b] (dL/g)	IEC(meq/g)	IV [b] (dL/g)	IEC(meq/g)
25°C	2.3	1.5	3.3	2.2
100°C	2.1	1.6	3.1	2.3
140°C	2.4	1.6	3.2	2.3
180°C	2.4	1.6	3.2	2.1
220°C	2.1	1.6	3.5	2.2
260°C	2.2	1.5	PS***	-

a): The BPSH membranes were treated at each temp. for 30 min. in air before Intrinsic Viscosity and IEC determination.

b): Intrinsic Viscosities were determined in NMP at 25°C, ***Partially soluble, indicating the thermal onset of branching.

Non-aqueous potentiometric titration was used to determine the content of proton-exchange groups (-SO_3H) quantitatively. The dried BPSH solutions in DMAC were titrated by standard tetramethyl ammonium hydroxide solution (~0.05N, in iso-propanol). One sharp end titration point was observed indicating a strong acid (-SO_3H) and base reaction. Assuming that all sulfonated monomer was incorporated into the polymer chain, the theoretical ion exchange capacity (IEC) for BPSH-40 and BPSH-60 are 1.7 and 2.4 meq/g, respectively, which are in good agreement with experimental data. (Table 2) All the above results indicate that SO_3Na and proton conductive groups, $-SO_3H$, could be introduced into polymer via a sulfonated monomer without any side reactions, which are often observed with post sulfonation methods. Moreover the ionic conductor was located on a deactivated phenyl ring, which should provide enhanced stability.

The stability of $-SO_3H$ groups was investigated by combination of non-aqueous potentiometric titration and intrinsic viscosity measurements. The free acid membrane, which is in the form that would be of greatest interest in proton exchange membranes for fuel cells, showed significantly more stability than might have been expected from small model molecule experiments. The molecular structure was stable for 0.5 hour up to 220°C at air, as proven by the stable IEC and intrinsic viscosity values (Table 2). It is argued that the deactivated phenyl rings will be better defined locations for the ion conductivity, since they are placed on the monomer prior to polymerization, and more stable to desulfonation since the anticipated intermediate carbocation required for desulfonation is more difficult to stabilize on such a sulfone deactivated ring.

The fully hydrated acid form membrane had a room temperature (25°C) proton conductivities of 0.11 and 0.17 S/cm for the 40/60 and 60/40 copolymers, respectively, while the conductivity of Nafion 1135 (IEC 0.91 meq/g) was 0.12 S/cm under the same conditions. The higher conductivity of 60% BPSH in comparison to Nafion 1135 is most likely a result of the greater IEC and water uptake of BPSH. Both factors were previously shown to affect the observed protonic conductivity of Nafion. The water uptake of BPSH was 70% by weight as opposed to a water uptake of 37% by the control Nafion membrane.

Conclusion

Poly(arylene ether sulfone)s containing up to 1.2 sulfonate groups per repeating unit (60 mole %) were successfully prepared by direct polymerization of the sulfonated activated halide using otherwise fairly similar "polysulfone" polymerization conditions. Tough acid form films obtained by solution casting method showed very high proton conductivity and good stability. The material is a candidate for new proton exchange membrane for fuel cells and the behavior of these materials in this capacity will be reported later.

Acknowledgements

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