

Synthesis and Characterization of 3,3'-Disulfonated-4,4'-dichlorodiphenyl Sulfone (SDCDPS) Monomer for Proton Exchange Membranes (PEM) in Fuel Cell Applications

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ABSTRACT: A systematic study of the synthesis and characterization of 3,3'-disulfonated-4,4'-dichlorodiphenyl sulfone (SDCDPS) monomer was conducted by varying reactant stoichiometries (molar ratios of 4,4'-dichlorodiphenyl sulfone (DCDPS) to SO₃ 1 : 2.2, 1 : 2.9, and 1 : 3.3), reaction temperature (90–120°C), and reaction time (4–6 h). The optimum synthesis batch process variables were 1 : 3.3 reactant molar ratio (DCDPS : SO₃) at 110°C for 6 h. In earlier studies, recrystallization of the "crude" disulfonated monomer from alcohol–water mixture was necessary to remove the monosulfonated and DCDPS impurities that lowered yield. However, in the current research, SDCDPS was successfully synthesized at nearly 100% conversion, which effectively eliminated the need for recrystallization. Recrystallization of SDCDPS from several alcohol–water mixtures (methanol–, ethanol–, and isopropanol–water mixtures) was investigated to compare product purities. Several characterization methods including proton NMR, HPLC, UV–visible, and fast atom bombardment mass spectroscopy confirmed that the crude SDCDPS was completely disulfonated and identical to recrystallized SDCDPS, without having any mo-

nosulfonated or starting material DCDPS impurities. Hence, it was demonstrated that the crude SDCDPS monomer by the current one-step process and the recrystallized SDCDPS monomer were identical. This optimized monomer synthesis has been used to scale up the SDCDPS and poly(arylene ether sulfone) random and statistical copolymers at controlled disulfonation (35 and 45 mol %) levels, which were then used to fabricate proton exchange membranes for fuel cell applications. The intrinsic viscosity data confirmed that high molecular weight film forming copolymers were synthesized. The calculated degree of disulfonations by proton NMR was in close agreement with target disulfonations. It may be concluded that this optimized SDCDPS synthesis eliminates the need for recrystallization, which would be expected to improve process economics. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 4595–4602, 2006

Key words: copolymerization; ionomers; poly(ether sulfones); one-step disulfonation; proton exchange membrane (PEM); fuel cells

INTRODUCTION

Sulfonated high-performance ion containing polymer "ionomers" can be produced by postsulfonation of polymeric precursors such as poly(arylene ether sulfone),¹ poly(benzimidazole),² and polyether ketones.³ These materials display phase-separated morphologies, which make them suitable for water

desalination, gas separations, and demanding applications requiring enhanced mechanical properties.^{4–6} The sulfonation reactions proceed by electrophilic aromatic substitution of the aromatic rings, using reagents such as SO₃ or chlorosulfonic acid. It is well recognized that another potential application for sulfonated aromatic copolymers is in proton exchange membrane (PEM) fuel cells. Nafion™, a perfluorinated sulfonic acid copolymer, is currently the state of art for such applications.^{7–9} Sulfonated aromatic copolymers may have several advantages such as higher mechanical strength, improved durabilities at higher temperatures in the fuel cell environment, and lower cost. These materials may be particularly advantageous in direct methanol fuel cells (DMFC) because of the lower methanol permeability compared to Nafion.

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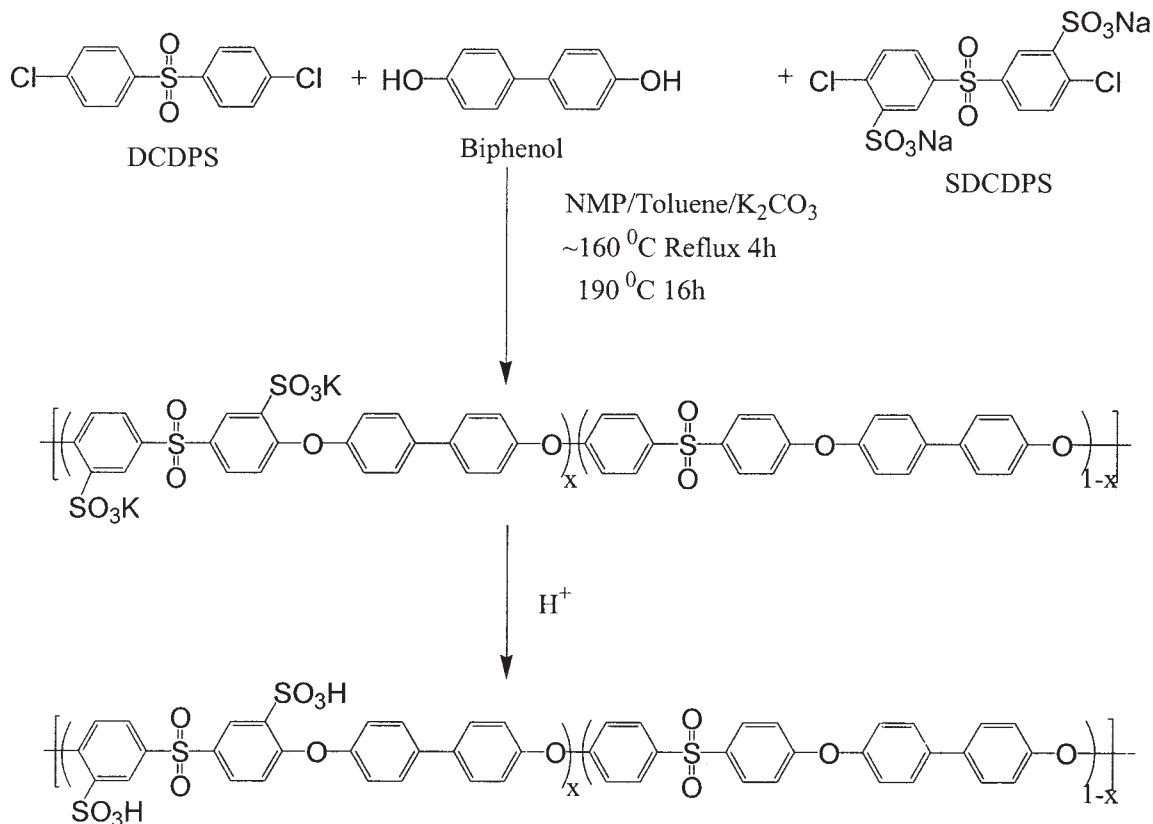


Figure 1 Synthesis of "BPSH" via the direct copolymerization route.¹⁰

We have recently described a direct statistical copolymerization route incorporating disulfonated activated aromatic halide monomers into poly(arylene ether sulfone) to prepare PEM materials (Fig. 1).^{11,12} This approach employs 3,3'-disulfonated-4,4'-dichlorodiphenyl sulfone (SDCDPS) copolymerized with nonsulfonated activated aromatic dihalides and bisphenols. The stoichiometric ratio of disulfonated to nonsulfonated repeat units can be accurately controlled to tailor the water uptake, conductivities, and mechanical properties of these film forming materials.^{11,13} The synthesis of SDCDPS was first reported by Robeson and Matzner¹⁴ and was later studied by Ueda *et al.*¹⁵ The synthesis procedure was further improved in our laboratory,^{10,16,17} but has never been investigated in the depth necessary to define several critical parameters required for the synthesis of larger scale quantities.

This paper describes the following: (1) a novel procedure for the synthesis and analysis of SDCDPS, with near quantitative conversion useful on a kilogram (or larger) scale, (2) identification of the impurities formed in the disulfonation reaction, and (3) demonstration of the synthesis of high molecular weight poly(arylene ether sulfone) copolymers using the disulfonated monomer prepared by this process.

EXPERIMENTAL

Reagents

Fuming sulfuric acid with a measured 27–33 wt % of sulfur trioxide (SO_3), sodium chloride, sodium hydroxide pellets, potassium carbonate, and toluene were obtained from Aldrich and used as received. Solvay Advanced Polymers Inc. provided high purity 4,4'-dichlorodiphenyl sulfone (DCDPS) monomer. The 4,4'-isopropylidenebisphenol (Bisphenol A) (Dow chemical) was recrystallized from toluene and dried under vacuum. *N*-Methyl-2-pyrrolidinone (NMP) (Fisher) was vacuum distilled from calcium hydride onto molecular sieves under vacuum, and then stored under nitrogen.

Disulfonation of DCDPS

The DCDPS (10 g, 0.0348 mol) and fuming sulfuric acid (SO_3) to DCDPS molar ratio were 1 : 2.2, 1 : 2.9, and 1 : 3.3. The amount of the electrophilic SO_3 in fuming sulfuric acid was determined by titration using 0.01N sodium hydroxide. The reagents were added to a 100-mL three-necked flask fitted with an overhead mechanical stirrer and nitrogen inlet and outlet, and were purged with nitrogen for several

minutes. The purge was then stopped during the reaction to minimize SO_3 losses. Disulfonation reactions were performed as a function of reaction time (4–6 h), temperature (room temperature and 90–120°C), and stoichiometries of the reactants. The reaction product was dissolved into a mixture of ice (50 g) and water (50 g). The sodium chloride (25 g) was dissolved with stirring into the solution when the solution temperature was about 65°C. The mixture was stirred, cooled to room temperature, and filtered. The product was redissolved in deionized water (100 g), and the pH of the solution was adjusted to 7 with 10N sodium hydroxide. The product was salted out by adding the sodium chloride (25 g) at about 65°C and filtered at room temperature. Finally, it was dried under vacuum at 160°C for 24 h.

Characterization methods

Monomer characterization

Chemical structures of both the SDCDPS monomer and the disulfonated copolymers were confirmed by proton NMR using a Varian Unity 400 spectrometer. All spectra were obtained from a 10% solution (w/v) in dimethylsulfoxide- d_6 solution at room temperature. High-performance liquid chromatography for the disulfonated monomers was conducted on a Beckman SystemGold chromatograph. The reversed phase column was obtained from the Restek Corp. Chromatograms were obtained by injecting 10 μL samples, which were prepared by first dissolving the samples in methyl alcohol. The mobile phase was acetonitrile–water (4 : 1 v/v). Further, purity studies of the SDCDPS monomer were conducted using a Shimadzu Model UV-1601 UV–visible spectrometer. The samples were dissolved in methanol to maintain several ppm solutions and absorbance data were generated. Fast atom bombardment mass spectroscopy (FAB-MS) in negative ion mode was obtained using JEOL-JMS HX110 dual focusing mass spectrometer. The low freezing point liquid matrix was 3-nitrobenzyl alcohol. Thermogravimetric analysis (TGA) was performed on a TA Instruments TGA Q 500. Dried SDCDPS monomer (5–10 mg) was evaluated over the range of 25–190°C at a heating rate of 10°C/min in air.

Copolymer characterization

Intrinsic viscosity measurements were performed in NMP at 25°C using a Cannon Ubbelohde viscometer. The proton NMR spectra were obtained as described earlier for the monomer characterization.

Model copolymerization

Disulfonated poly(arylene ether sulfone) copolymers were achieved with various degrees of disulfonation

(35–45 mol % SDCDPS) via direct copolymerization of SDCDPS, DCDPS, and 4,4'-biphenol (BP), as reported by Sankir.¹⁰ The DCDPS (2.5866 g, 0.0090 mol), SDCDPS (2.3826 g, 0.0049 mol), BP (2.5804 g, 0.0139 mol), and potassium carbonate (15% excess, 2.2025 g) were transferred to a three-necked flask equipped with a mechanical stirrer, a nitrogen inlet, and a Dean Stark trap. Dry NMP (15 mL) was introduced to provide 35% (w/v) solid concentration, and the ratio of NMP to toluene (v/v), an azeotroping agent, was 2 : 1. The reaction mixture was refluxed for 4 h at 150°C to complete the dehydration process. The reaction temperature was slowly increased to 190°C for 16 h, after gradual removal of the toluene. The viscous reaction product was cooled and diluted with NMP (10 mL) and precipitated in deionized water (500 mL) as swollen fibers. After being washed several times with deionized water, the precipitated copolymer was transferred to boiling deionized water where the salts were extracted for 4 h. The copolymer was then washed several times with deionized water and dried in a vacuum oven at 120°C for 24 h.

RESULTS AND DISCUSSION

The disulfonation reaction was found to be mostly affected by the reactant stoichiometries, reaction temperature, and time. The desired amount of fuming sulfuric acid based on the actual titrated measurement of the SO_3 content in fuming sulfuric acid was the most important optimization variable. It was observed that the crude disulfonated product salted out with some monosulfonated impurity and starting material with the low reactant ratios, *e.g.*, moles of DCDPS to SO_3 were 2.2 and 2.9. Theoretically, these ratios were enough for complete disulfonation. However, experimentally, this was only achieved when the reactant ratio was about 3.3. It was obvious that stoichiometry was easily upset by SO_3 loss during the earliest conducted reaction and possibly also by material transfer including weighing step prior to reaction. However, the use of 1.3 mol excess of SO_3 containing fuming sulfuric acid produced products of essentially 100% conversion. The ^1H NMR spectra, as a function of reactant ratios, confirming this are provided in Figure 2.

The reaction temperature was another optimization variable. Based on the literature and our earlier studies, it was generally varied in the range of 90–120°C. Later, some experiments were conducted at room temperature, with the optimized reactant molar ratio of 1 : 3.3 (DCDPS : SO_3). The reaction progress was monitored and the results were summarized (Table I) in terms of the observed impurities by ^1H NMR. Subsequently, all disulfonation reactions were conducted at 110°C. The disulfonation reaction at 110°C with 1 : 3.3 reactant mol ratio was repeated for 4–6 h and always produced only disulfonated product. Therefore, it

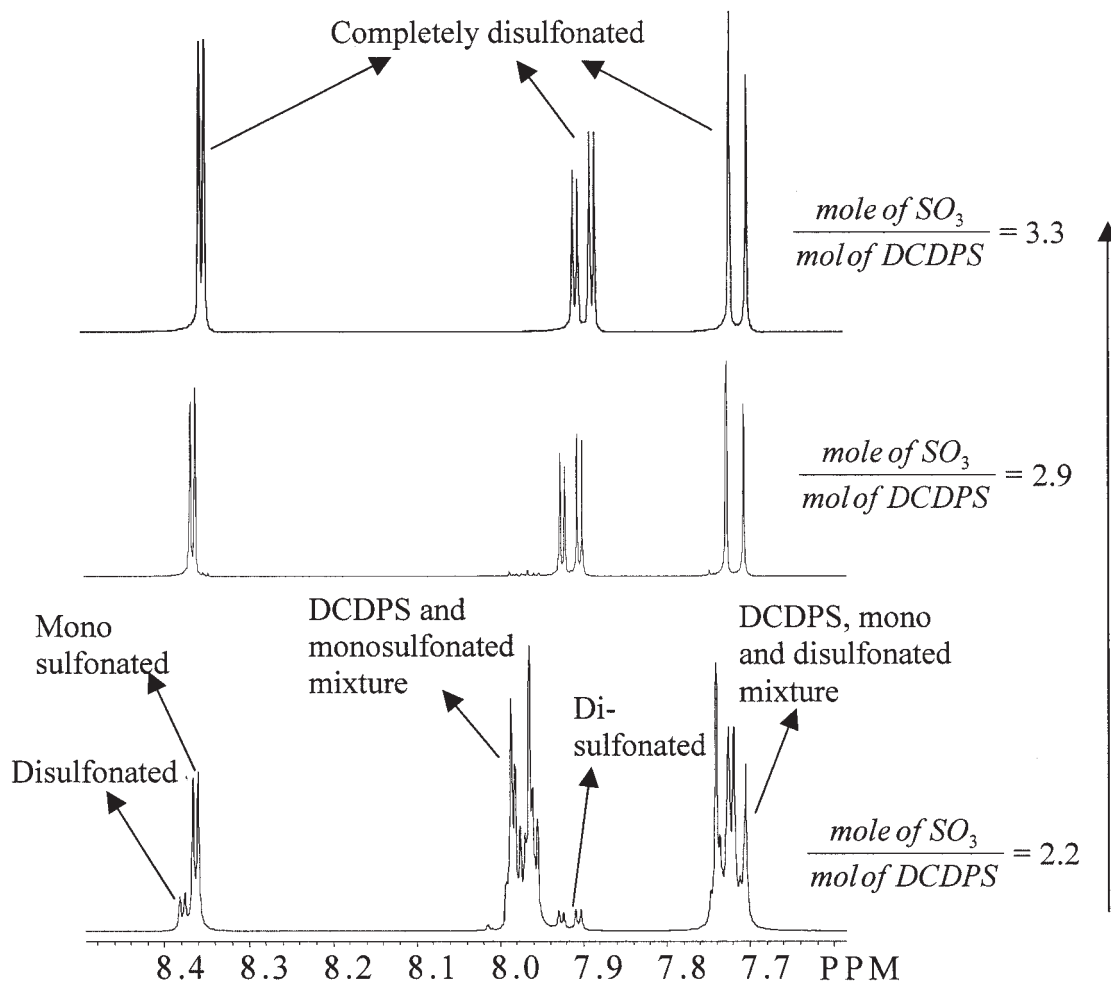


Figure 2 Effect of reactant ratio on disulfonation reaction: mixture of monosulfonated, disulfonated product, and starting material disappear gradually with increasing reactant ratio.

may be concluded that the best conditions for the disulfonation reaction were at 110°C with 1 : 3.3 reactant ratio for 6 h.

The sulfonic acid moieties were converted to their sodium salt form after the disulfonation reaction to isolate the product. The excess acid in the isolated product was titrated slowly with sodium hydroxide

until the product salted out. The final SDCDPS was dried for 24 h at 160°C to remove all of the water. TGA after this drying treatment shows only about 0.5% loss, which indicates that almost all of the water was removed by the drying step (Fig. 3).

Recrystallization of the "crude" disulfonated monomer from various alcohol–water mixtures was earlier performed to remove the monosulfonated and DCDPS impurities. However, under the condition described earlier, one does not observe monosulfonated product or starting material. Recrystallization was performed to compare the polymerizability of the recrystallized and crude products. The major drawback with the recrystallization is that yield decreases markedly to about 50–70% for various alcohol–water mixtures such as methanol–water, ethanol–water, and isopropanol–water. The chemical structure of the disulfonated monomer was confirmed and compared with its recrystallized form by FAB-MS in the negative ion mode, proton NMR, HPLC, and UV spectroscopy.

TABLE I
Proton NMR of the Disulfonation Reaction After 6 h
Reaction at 1 : 3.3 DCDPS : SO₃ Stoichiometry

Reaction Temperature (°C)	Starting material DCDPS	Monosulfonated DCDPS	Disulfonated DCDPS
25–28	MP	O	O
90	O	O	O
100	NO	O	O
110	NO	NO	DP
120	NO	NO	DP

MP, major product; O, observed, NO, not observed; and DP, desired product.

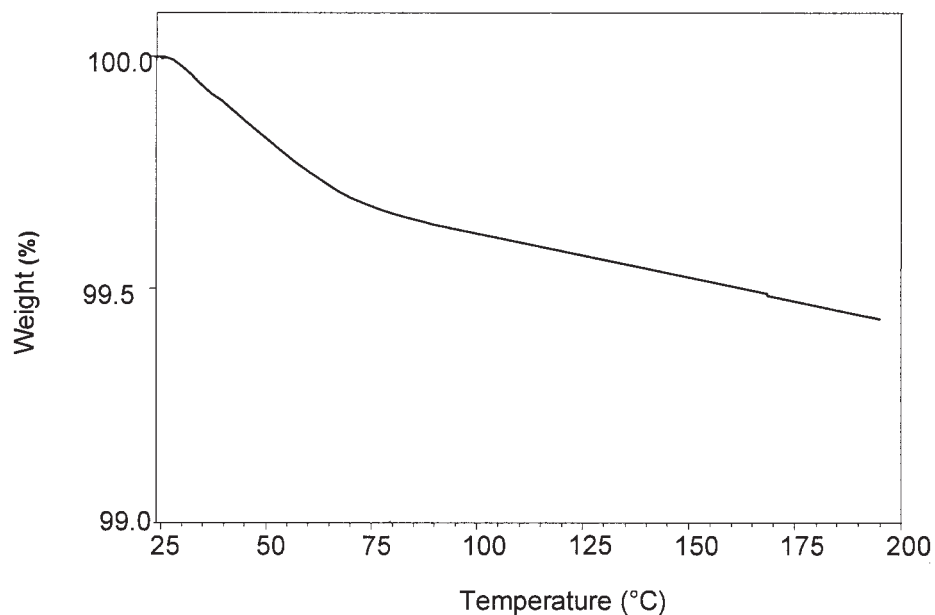


Figure 3 TGA of SDCDPS monomer dried at 160°C for 24 h indicates about 0.5 weight percent water.

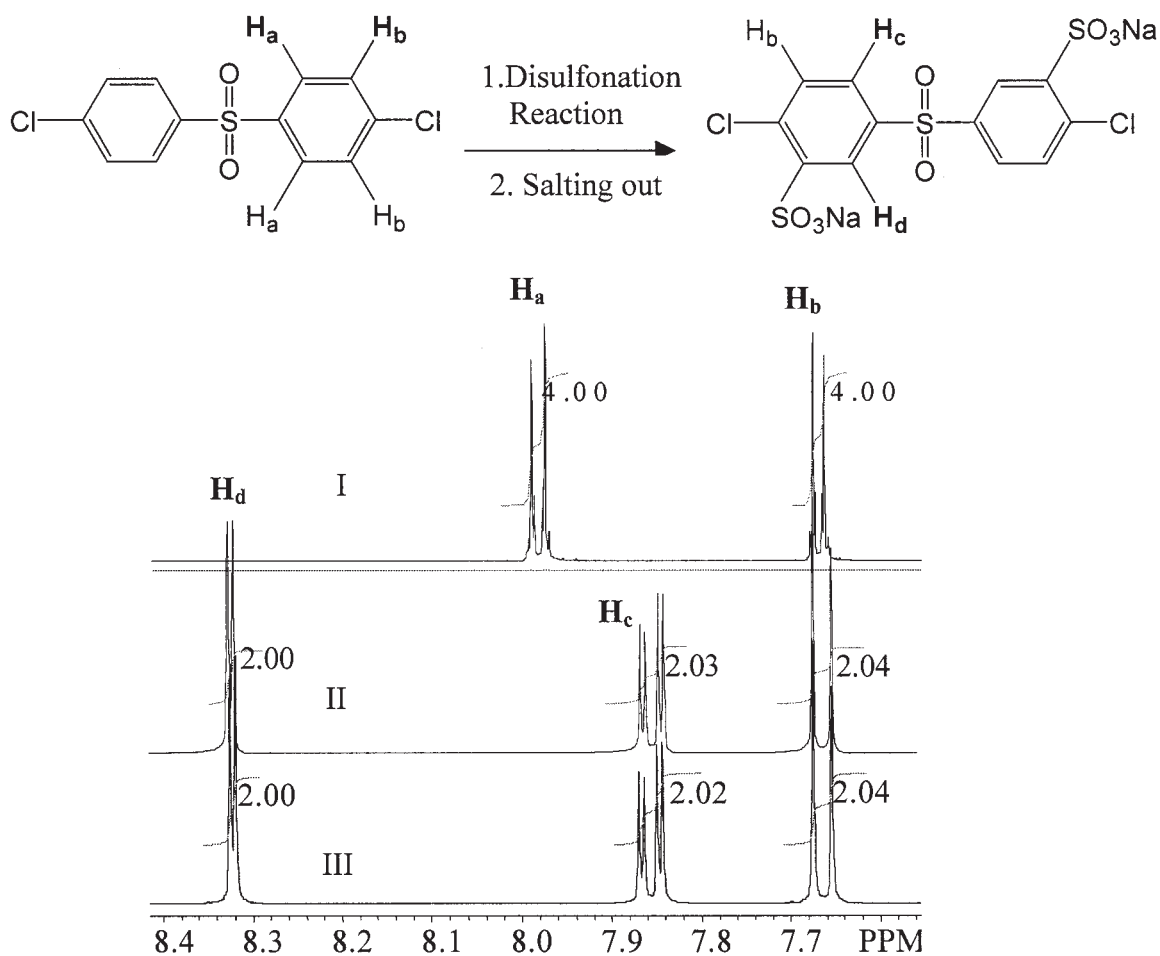


Figure 4 ¹H NMR spectrum of starting material DCDPS (I), crude SDCDPS monomer (II), and recrystallized SDCDPS monomer (III): the peak incorporated at about 8.32 ppm and integration values confirm disulfonation.

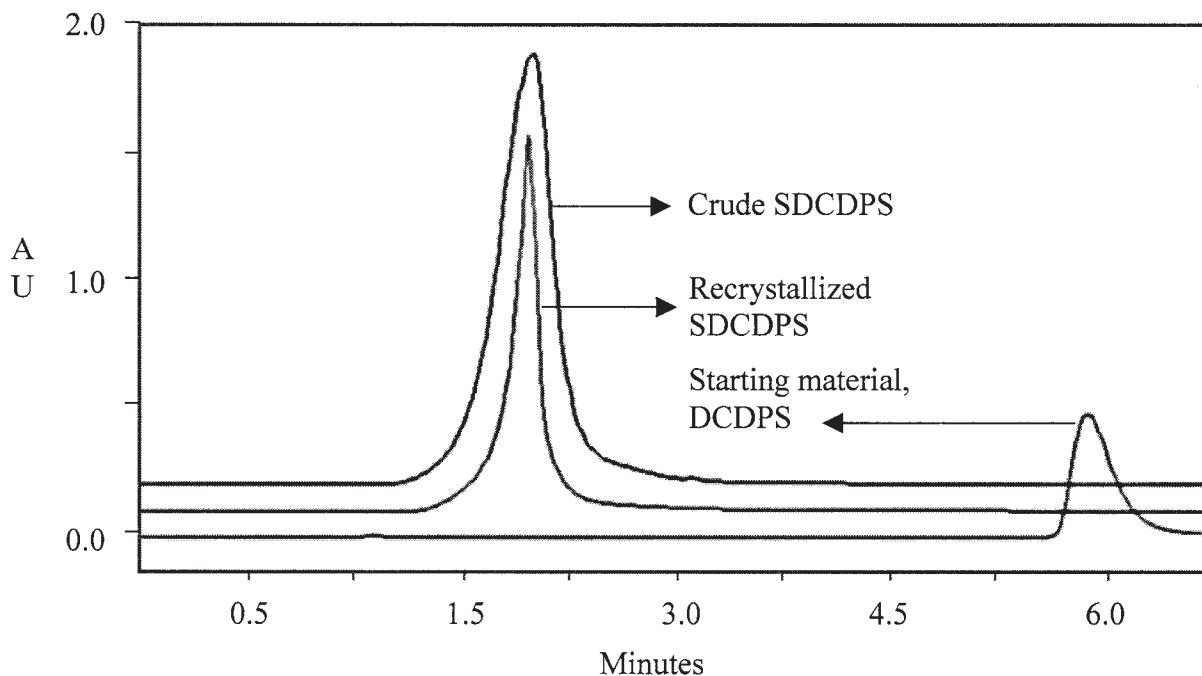


Figure 5 HPLC chromatograms for crude SDCDPS monomer, recrystallized SDCDPS monomer, and the starting material DCDPS.

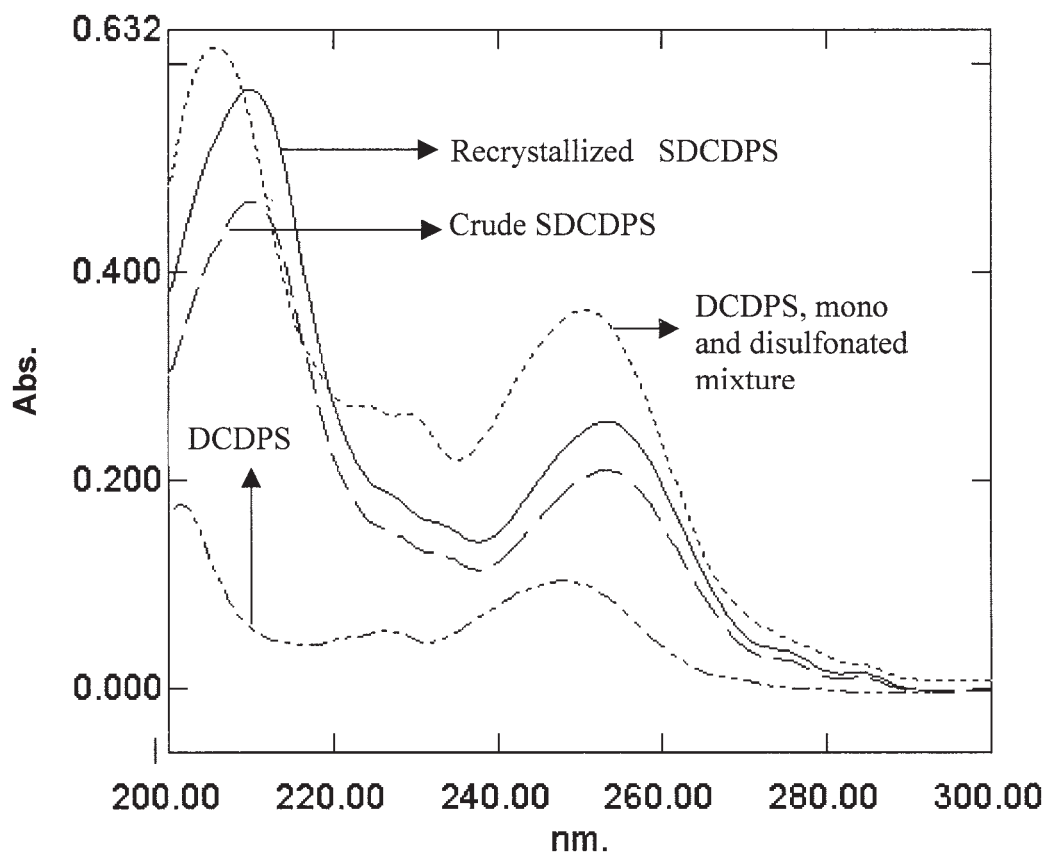


Figure 6 UV absorbance spectra of crude SDCDPS monomer, recrystallized SDCDPS monomer, the starting material DCDPS, and mixture of all when a deficient amount of SO_3 was used.

TABLE II
Two Fragmentation Characteristics of the Disulfonated Monomer

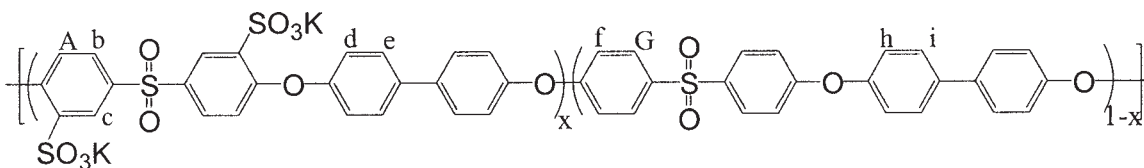
SDCDPS (M)	Fragmentation I	Fragmentation II
C ₁₂ H ₆ Cl ₂ Na ₂ O ₈ S ₃ MW : 491.2542 g/mol	(M-1Na) ⁻	(M-2Na+1H) ⁻
Molecular weights from FAB-MS	468.263	446.281

The proton NMR for both the crude and recrystallized monomer and starting material is shown in Figure 4. The new peak (H_d) incorporated at about 8.3 ppm indicates the proton next to the SO₃Na and confirms the disulfonation. The meta proton with respect to chlorine (H_b) atom was not affected much from sulfonation and remained in same position as in the DCDPS structure. However, the proton labeled as H_c was affected by the SO₃Na moieties and shifted from about 8 to 7.85 ppm. It should be pointed out that all these characteristic peaks were observed for both one-step and recrystallized products.

Reversed phase HPLC in which the stationary phase is nonpolar and mobile phase is relatively polar was used to measure the retention times of the crude SDCDPS, recrystallized SDCDPS, and starting material DCDPS. The most polar components among these materials eluted first and were either the crude or recrystallized SDCDPS. The least polar component, the starting material DCDPS, eluted last (Fig. 5). The crude and recrystallized SDCDPS showed exactly same retention time. However, crude SDCDPS peak was slightly broader than that of recrystallized SDCDPS. This may be due to the some associated excess sodium chloride from the salting out step, which relatively decreased during the recrystallization step.

A blue shift due to the disulfonation was observed by UV spectroscopy. The UV spectrometric determination of crude SDCDPS, recrystallized SDCDPS, and the starting DCDPS is shown in Figure 6. It can be noted that both crude and recrystallized SDCDPS show exactly the same UV absorption characteristics.

FAS-MS is a soft ionization method for polar and labile materials. The disulfonated monomer has two sulfonated moieties, which afforded two major minus



$$\text{Mole percent of sulfonation} = (A/2) * 100 / (A/2 + G/4) = 34.9 \%$$

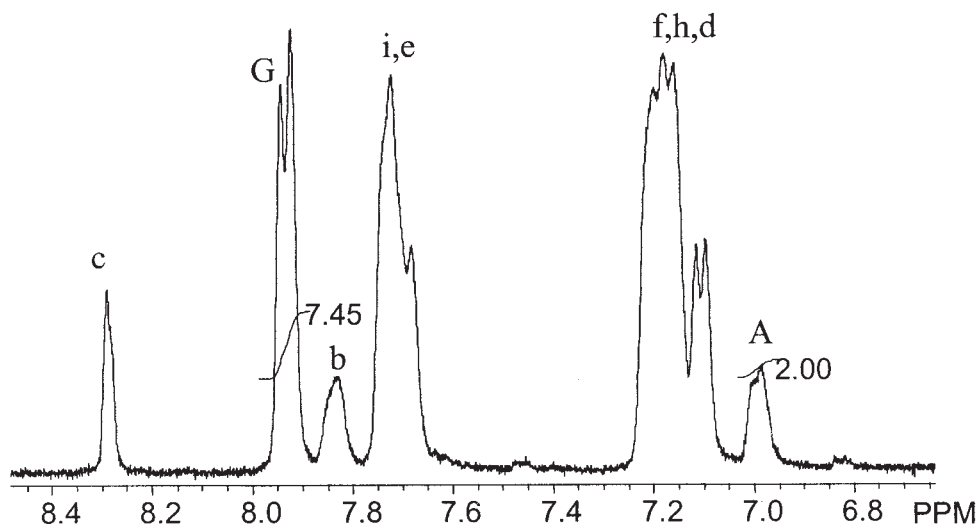


Figure 7 ¹H NMR spectra of disulfonated poly(arylene ether sulfone) copolymer synthesized with SDCDPS using the current process.

TABLE III
Intrinsic Viscosity and Mole Percent Disulfonation of the BPS Copolymers, Which Indicate High Molecular Weight Copolymers Were Achieved

Copolymer	$[\eta]_{25^\circ\text{C}}^{\text{NMP}}$ (dL/g)	Mole percent sulfonation ($^1\text{H NMR}$)
BPS-35	1.1	34.9
BPS-45	1.2	44.5

charged fragmentations. The results are summarized in Table II. The first fragmentation labeled as $(\text{M}-1\text{Na})^-$ was due to the loss of one sodium atom from entire monomer structure. Another characteristic fragmentation was due to the loss of two sodium atoms and incorporation of a proton, which maintains the minus one charge $(\text{M}-2\text{Na}^+\text{H})^-$. Both the crude and recrystallized disulfonated monomers showed the same characteristics, indicating that the crude and recrystallized monomers have same chemical structure. Otherwise, the possible impurities such as monosulfonated monomer and starting material DCDPS would result in deviation in the obtained molecular weight of disulfonated monomer from FAS-MS. However, the two fragmentation patterns showed an exact agreement with the calculated molar mass of the disulfonated monomer.

The disulfonated monomer process described earlier was successfully scaled up at Hydrosize Inc. to kilogram quantities. The optimized monomer has been used to scale up poly(arylene ether sulfone) copolymers that are of interest as PEM for fuel cell applications. The proton NMR spectrum of the copolymer is shown in Figure 7. The intrinsic viscosities confirmed that high molecular weight film forming copolymers were synthesized (Table III).

CONCLUSIONS

Synthesis conditions for generating SDCDPS from DCDPS and fuming sulfuric acid were systematically studied and optimized. The best disulfonation reaction was achieved using a 1 : 3.3 reactant mol ratio

(DCDPS : SO_3) at 110°C for 6 h. The salted out product was isolated always in disulfonated form without having any monosulfonated or starting material DCDPS impurities. Several characterization methods confirmed that crude and recrystallized SDCDPS monomers were identical. The scale up of the SDCDPS monomer and high molecular weight disulfonated poly(arylene ether sulfone copolymer) for making PEM in fuel cell applications at kilogram quantities has been demonstrated. The disulfonation reaction product is of polymerization purity without the need for a recrystallization step, which one may conclude is important for process economics.

References

1. Quentin, J. P. (Rhone-Poulenc). U.S. Pat. 3,709,841 (1973).
2. Glipa, X.; Haddad, M.E.; Jones, D.; Roziere, J. *Solid State Ionics* 1997, 97, 33.
3. Alberti, G.; Casciola, M.; Massinelli, L.; Bauer, B. *J Membr Sci* 2001, 185, 73.
4. Lundberg, R. D. In *Encyclopedia of Polymer Science Engineering*, Kroschwitz, J. I., Ed.; Wiley: New York, 1987.
5. Fitzgerald, J. J.; Weiss, R. A. *J Macromol Sci Rev Macromol Chem Phys* 1998, C28, 99.
6. Hajatdoost, S.; Yarwood, J. *J Chem Soc Faraday Trans* 1997, 93, 1613.
7. Jones, D. J.; Roziere, J. *J Membr Sci* 2001, 185, 41.
8. Kerres, J. A. *J Membr Sci* 2001, 185, 3.
9. Jorissen, L.; Gogel, V.; Kerres, J.; Garche, J. *J Power Sourc* 2002, 105, 267.
10. Sankir, M.; Bhanu, V. A.; Ghassemi, H.; Wiles, K. B.; Hill, M. H.; Harrison, W.; Sumner, M.; Glass, T. E.; Riffle, J. S.; McGrath, J. E. *Polym Prepr (Am Chem Soc Div Polym Chem)* 2003, 44, 1079.
11. Harrison, W. L. Ph.D. Dissertation, Virginia Tech, 2002.
12. Harrison, W. L.; Wang, F.; Mecham, J. B.; Bhanu, V. A.; Hill, M.; Kim, Y. S.; McGrath, J. E. *J Polym Sci Part A: Polym Chem* 2003, 41, 2264.
13. Wang, F.; Hickner, M.; Kim, Y. S.; Zawodzinski, T. A.; McGrath, J. E. *J Membr Sci* 2002, 197, 231.
14. Robeson, L. M.; Matzner, M. (Union Carbide). U.S. Pat. 4,380,598 (1983).
15. Ueda, M.; Toyota, H.; Ouchi, T.; Sugiyama, J.; Yonetake, K.; Masuko, T.; Teramoto, T. *J Polym Sci Part A: Polym Chem* 1993, 31, 853.
16. Hickner, M. A.; Ghassemi, H.; Kim, Y. S.; Einsla, B. R.; McGrath, J. E. *Chem Rev* 2004, 104, 4587.
17. Wang, F.; Hickner, M. A.; Ji, Q.; Harrison, W. L.; Mecham, J. B.; Zawodzinski, T. A.; McGrath, J. E. *Macromol Symp* 2001, 175, 387.