



## Purity characterization of 3,3'-disulfonated-4,4'-dichlorodiphenyl sulfone (SDCDPS) monomer by UV–vis spectroscopy

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### ABSTRACT

The purity of the disulfonated monomer, 3,3'-disulfonated-4,4'-dichlorodiphenyl sulfone (SDCDPS), is very important for obtaining high molecular weight disulfonated poly(arylene ether sulfone) random or block copolymers, which are promising candidates for proton exchange membrane (PEM) fuel cells. For commercialization purposes, direct use of unrecrystallized SDCDPS monomer with known purity in the copolymerization favorably influences its economics relative to the traditional recrystallization purification process. In this paper, a novel method to characterize the purity of the prepared unrecrystallized SDCDPS has been developed using UV–vis spectroscopy. The purity of the comonomer was determined from a Beers Law calibration curve developed using a highly purified SDCDPS sample. High molecular weight poly(arylene ether sulfone) random copolymers, based on this unrecrystallized SDCDPS monomer, 4,4'-dichlorodiphenyl sulfone (DCDPS), and 4,4'-biphenol monomers, were successfully synthesized. The molecular weight obtained from gel permeation chromatography (GPC) ( $M_n > 45 \text{ kg mol}^{-1}$ ) was high enough to allow tough films for PEMs to be solvent cast. This confirmed that the purity characterization method was relatively accurate and applicable. The effect of storage and drying time of SDCDPS were also studied using Beer's Law plots.

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### 1. Introduction

A large number of novel ion-containing copolymers have been extensively investigated for proton exchange membranes (PEMs) to provide attractive alternatives to the currently commercialized perfluorosulfonic acid, Nafion<sup>®</sup> [1–3]. Sulfonated poly(arylene ether) materials, such as poly(arylene ether ketone)s and poly(arylene ether sulfone)s, are attractive for use in PEMs because of their well known oxidative and hydrolytic stability under a fuel cell's harsh conditions [4]. Introduction of the sulfonic acid groups to the polymer backbone has been achieved by either post-sulfonation of commercially available copolymers or direct copolymerization of sulfonated monomers [1]. It has been widely accepted that the direct copolymerization method has advantages over the post-modification method, including its easy control of the position and degree of sulfonation, high acidity, and the ease of minimizing side reactions. Recently, the applicability of this approach has been extended to other application areas such as reverse osmosis water purification [5,6] and polymeric transducers [7].

The disulfonated monomers used in the direct copolymerizations were synthesized via electrophilic aromatic substitution with fuming sulfuric acid. The monomer 3,3'-disulfonated-4,4'-dichlorodiphenyl sulfone (SDCDPS) is the most important example. SDCDPS was first reported by Robeson and Matzner [8] in a patent for its flame retarding properties and was subsequently studied by Ueda et al. [9]. Our group modified its purification and characterization procedure and used it to directly copolymerize SDCDPS with 4,4'-dichlorodiphenyl sulfone (DCDPS) and 4,4'-biphenol to synthesize disulfonated poly(arylene ether sulfone)s for use as proton exchange membranes [10,11]. Thereafter, similar procedures were used to synthesize several different disulfonated monomer structures for use in the aforementioned applications (Fig. 1) [12–14].

It is well known from the Carothers equation that the purity of the disulfonated monomer is very important in obtaining high molecular weight copolymers using step-growth copolymerization. A systematic study of the synthesis and characterization of SDCDPS monomer ensured that the possible monosulfonated and starting material DCDPS impurities could be avoided when following the standard synthetic procedure [15]. The only impurities that remained in the product were water and sodium chloride, which was used in excess to salt out the crude sulfonated monomer. Traditionally, sodium chloride can be removed by recrystallization of the product in a mixture of isopropanol and water, or other

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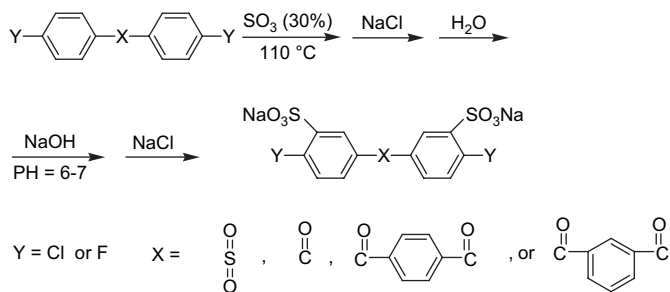


Fig. 1. Synthetic scheme of disulfonated monomers with several different structures.

alcohol/water systems. The recrystallization was typically repeated two to three times to increase monomer purity. This recrystallization method was effective in lab-scale experiments but would not be economical for mass production because it substantially decreases the monomer yield and requires solvent, time, and energy.

In this paper, a novel method to characterize the purity of unrecrystallized SDCDPS was developed using UV–vis spectroscopy. A Beer's Law calibration curve was developed by first measuring the absorbance of several highly pure SDCDPS/methanol dilute solutions with known concentrations, then plotting the absorbance vs. concentrations of these solutions. The purity of the unrecrystallized SDCDPS was easily determined from the Beer's Law calibration curve. Because the SDCDPS monomer is sensitive to moisture, the effect of storage time and drying time were also studied. Disulfonated poly(arylene ether sulfone) model random copolymers (Fig. 2) with 35% and 40% degree of sulfonation were synthesized using the unrecrystallized SDCDPS monomer with determined purity to confirm the accuracy and applicability of this characterization method. Gel permeation chromatography (GPC) results showed that copolymers with molecular weights higher than  $45 \text{ kg mol}^{-1}$  were obtained, which was high enough to form tough membranes for PEM fuel cells [16]. The purpose of this paper is to provide an accurate and practical way to characterize the purity of SDCDPS because an increasing number of novel random and block copolymer PEM materials can utilize this sulfonated monomer [11,13,16–29]. This would be especially useful for scale up purposes and could also be used to characterize other similar disulfonated monomer structures like those illustrated in Fig. 1.

## 2. Experimental

### 2.1. Materials

High purity DCDPS monomer was kindly provided by Solvay Advanced Polymers Inc and was dried under vacuum at  $60 \text{ }^\circ\text{C}$  for 24 h prior to use. Fuming sulfuric acid with 27–33 wt% of sulfur

trioxide ( $\text{SO}_3$ ) was purchased from Aldrich and used as received. Crude SDCDPS, which had been scaled to kilogram quantities, was provided by Hydrosize Inc and was dried under vacuum at  $160 \text{ }^\circ\text{C}$  for at least 48 h before use. Monomer grade, high purity 4,4'-biphenol (BP) was obtained from Eastman Chemical and dried under vacuum at  $60 \text{ }^\circ\text{C}$  for 24 h before use. Dimethylacetamide (DMAc, Aldrich) was vacuum-distilled from calcium hydride onto molecular sieves and stored under nitrogen before use. Potassium carbonate (Aldrich) was dried under vacuum at  $120 \text{ }^\circ\text{C}$  for 24 h before use. Toluene, methanol, isopropanol, sodium chloride, and sodium hydroxide pellets were obtained from Aldrich and used as received.

### 2.2. Synthetic procedures

#### 2.2.1. Synthesis and purification of SDCDPS monomer

The synthesis of SDCDPS followed the synthetic procedure reported from our laboratories and others in the literature [10,11,15]. The reaction conditions were chosen to ensure that the monosulfonated and starting material impurities were avoided. DCDPS (30 g) and fuming sulfuric acid (60 mL, 30%  $\text{SO}_3$ ) (molar ratio was 1:3.3) were added to a 250-mL three-necked flask equipped with an overhead mechanical stirrer, nitrogen inlet and condenser. The reaction mixture was heated to  $110 \text{ }^\circ\text{C}$  for 6–7 h. Isolation of the product was achieved using a standard procedure which included salting out by sodium chloride, neutralization with 10 N sodium hydroxide, and again salting out with sodium chloride (Fig. 1). The SDCDPS was purified by recrystallization with a mixture of deionized water and isopropyl alcohol (IPA) (3/7, v/v) to remove sodium chloride, which was the only impurity. Recrystallization was repeated up to six times until no absorption intensity change was observed on the UV–vis spectrum when measured at the same solution concentration. The SDCDPS monomer was dried under vacuum at  $160 \text{ }^\circ\text{C}$  for at least two days and used immediately upon removal from the oven, unless noted otherwise.

#### 2.2.2. Synthesis of disulfonated poly(arylene ether sulfone) (BPS) model random copolymers

The crude SDCDPS monomer obtained from Hydrosize Inc. was directly used to synthesize the disulfonated poly(arylene ether sulfone) model random copolymers. The purity determined from the Beer's Law calibration curve for the batch was  $91.4\% \pm 0.5\%$  following the procedure described in Section 2.3.2. Disulfonated poly(arylene ether sulfone) random copolymers with 35 mol% (BPS35) and 40 mol% (BPS40) degree of sulfonation were synthesized by copolymerization of SDCDPS, DCDPS, and BP monomers. As an example, the following monomer feed was used for synthesis of BPS35: unrecrystallized SDCDPS (5.3904 g, 10.029 mmol), DCDPS (5.3488 g, 18.626 mmol), and BP (5.3357 g, 28.654 mmol). The synthetic procedure was the same as reported previously [10,11].

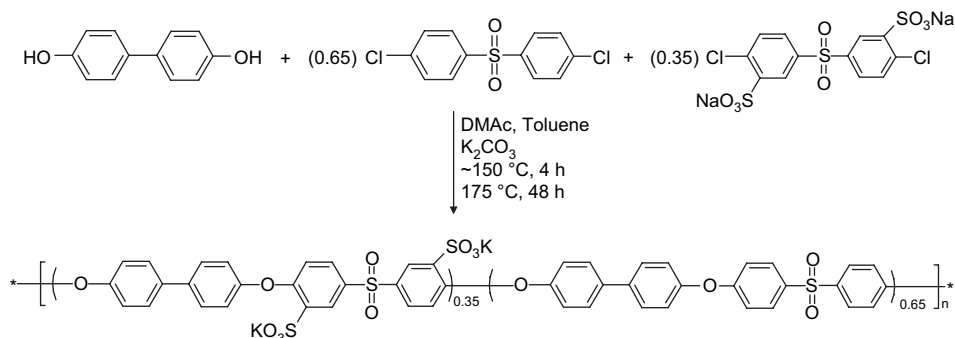


Fig. 2. Synthetic scheme for 35 mol% disulfonated poly(arylene ether sulfone) random copolymer.

### 2.3. Characterization

#### 2.3.1. Monomer and copolymer characterization

Proton nuclear magnetic resonance ( $^1\text{H}$  NMR) analyses were conducted with a Varian Unity 400 NMR spectrometer to confirm the chemical structures of both the SDCDPS monomer and the disulfonated copolymers. Spectra were obtained using  $\text{DMSO-}d_6$  as the solvent. Intrinsic viscosities (I.V.) and the molecular weights of the copolymers were characterized by gel permeation chromatography (GPC) using polystyrene as a standard. GPC (also known as SEC) experiments were performed on a liquid chromatograph equipped with a Waters 1515 isocratic HPLC pump, Waters Auto-sampler, Waters 2414 refractive index detector and Viscotek 270 dual detector.  $\text{LiBr/NMP}$  (0.05 M) was used as the mobile phase. The column temperature was maintained at  $60^\circ\text{C}$  because of the viscous nature of NMP. Both the mobile phase solvent and sample solution were filtered before introduction to the GPC system.

#### 2.3.2. Procedure for SDCDPS monomer purity characterization by UV-vis spectroscopy

Purity characterizations of the SDCDPS monomer were carried out using a Shimadzu Model UV-1601 UV-vis spectrometer. The first step was to determine the molar absorptivity ( $\epsilon$ ) of SDCDPS monomer by Beer's Law:  $A = \epsilon bc$ , in which  $A$  is the absorbance measured from the UV-vis spectrum,  $c$  is the dilute solution concentration ( $\text{mol L}^{-1}$ ), and  $b$  is the path length of the sample (1 cm). The procedure was as follows: pure SDCDPS monomer was obtained by recrystallization as described earlier using IPA/DI  $\text{H}_2\text{O}$  as the recrystallization solvent mixture. This recrystallization was performed up to six times until the UV-vis absorption had no change when measured at the same concentration. The completely dried, pure SDCDPS monomer (61.6 mg) was dissolved in methanol in a 100-mL volumetric flask to prepare solution 1 with a concentration of  $1.254 \times 10^{-3} \text{ mol L}^{-1}$ . Exact volumes in the range of 2–10 mL of solution 1 were transferred to a 250-mL volumetric flask and then diluted with methanol to prepare dilute solutions with various known concentrations. UV-vis absorbance data generated from these dilute solutions were used to develop the Beer's Law calibration curve, which was a straight line in the low absorbance range ( $<1.5$ ). The slope of this linear plot was the molar absorptivity ( $\epsilon$ ) in Beer's Law. Once the Beer's Law plot was constructed, the purity of the unrecrystallized SDCDPS sample was easily determined by measuring the UV-vis absorbance of a sample solution with known concentration. The concentration of the sample solution was chosen such that the absorbance fell within the linear range of the calibration curve. Each measurement was repeated at least three times, and the average values were recorded.

### 3. Results and discussion

An electrophilic aromatic substitution reaction was employed to synthesize SDCDPS, using 30% fuming sulfuric acid as the sulfonation agent. Possible impurities that could have resulted when synthesizing SDCDPS were the monosulfonated byproduct, unsulfonated starting material, and sodium chloride. The monosulfonated byproduct and residual starting monomer (DCDPS) impurities were effectively avoided by following our previously reported synthesis conditions [15]. The absence of these impurities was confirmed by examining chemical shifts and integrations of the  $^1\text{H}$  NMR peaks. However, sodium chloride was used in excess to salt out the SDCDPS from the water and thus was the only impurity present in the product. Several recrystallizations from an IPA/ $\text{H}_2\text{O}$  solvent mixture were usually used to purify the SDCDPS monomer. This procedure worked well in lab-scale experiments, but it substantially decreased the product yield because of the high solubility

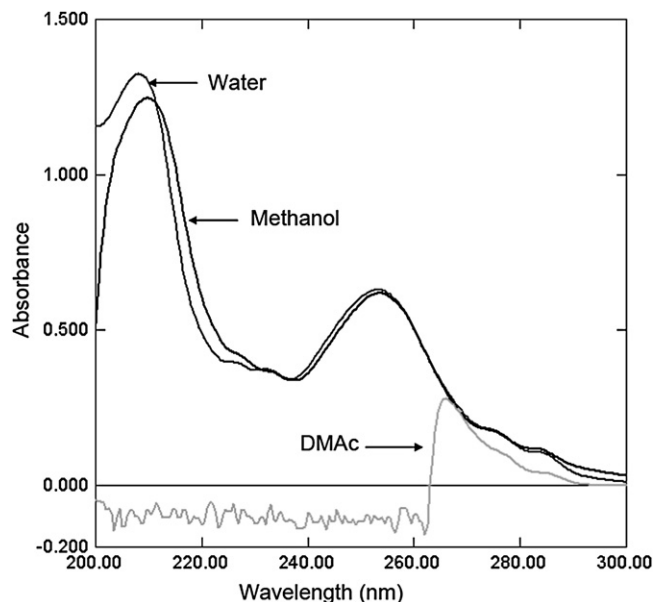


Fig. 3. UV-vis spectra of SDCDPS dilute solutions using different solvents.

of SDCDPS in water. It also wasted time, solvent, and energy, and would be undesirable for scaled up systems.

Clearly, if the purity of the sulfonated monomer can be accurately determined, it is desirable to use the unrecrystallized SDCDPS directly in the copolymerization because sodium chloride has no influence on the nucleophilic step-growth copolymerization reaction. UV-vis spectroscopy is a very sensitive method for quantitatively determining the concentration of a solution using Beer's Law if the molar absorptivity of the sample is available. The SDCDPS monomer dilute solution had two absorption peaks in the UV-vis range (wavelength: 210 nm and 254 nm), which allowed the use of this technique to determine the monomer's purity. For consistency, the peak at 210 nm was used for all following measurements.

Solvent choice is an important consideration because it can affect both the peak position and intensity of the UV-vis spectra.

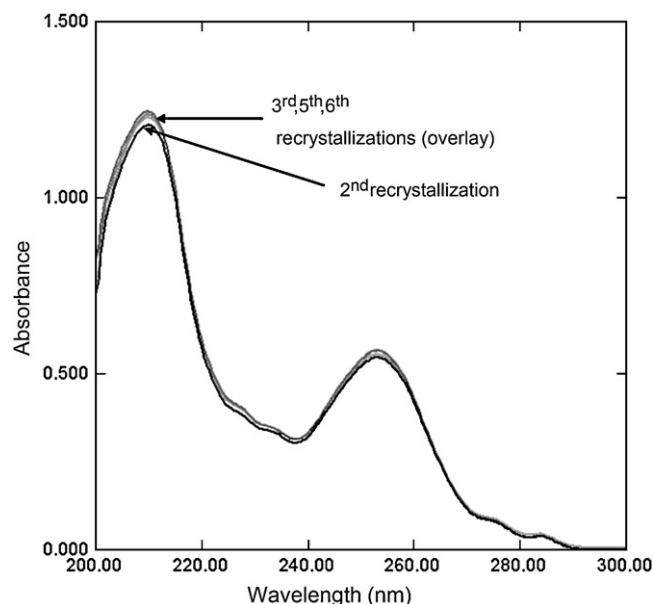


Fig. 4. Effect of the number of recrystallization times on the absorbance at the same concentration values (e.g. after second recrystallization, SDCDPS still contained  $2.6\% \pm 1\%$  salt).

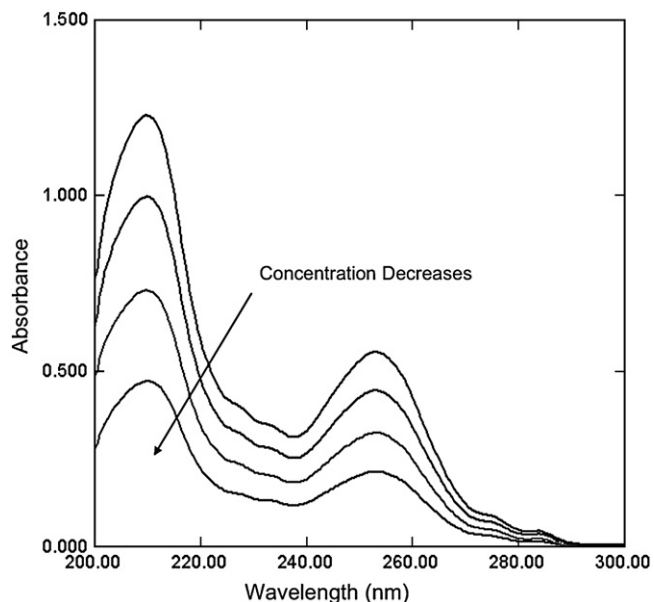


Fig. 5. The UV-vis absorbances of SDCDPS solutions with different concentrations were used to develop the calibration curve.

Three good solvents for SDCDPS (water, methanol, and DMAc) were tested, and the UV-vis spectra were obtained (Fig. 3.). The SDCDPS sample dissolved in DMAc did not generate a good spectrum. Good spectra were obtained when water or methanol were used as the solvent. Methanol was chosen as the solvent for all measurements because it was observed that volumetric solutions could be prepared more accurately than with water.

To develop the Beer's Law calibration curve, a very pure SDCDPS sample was required. SDCDPS was purified by recrystallization from an IPA/H<sub>2</sub>O (7/3, v/v) solvent mixture, and the process was repeated up to six times. The purity of the SDCDPS was monitored using UV-vis spectra. By keeping the sample concentrations of all measurements the same, it could be determined that the purity was unchanged after the third recrystallization because the absorbance was no longer changing (Fig. 4). Although the first recrystallization removed most of the salt, at least two more recrystallizations were required to remove all of the salt. The pure SDCDPS (after the sixth recrystallization) was used to prepare solution 1 with concentration  $1.254 \times 10^{-3} \text{ mol L}^{-1}$ , and then exact volumes (2–10 mL) of solution 1 were transferred to 250-mL volumetric flasks and diluted with methanol to prepare dilute solutions with various known concentrations. The absorbance of the

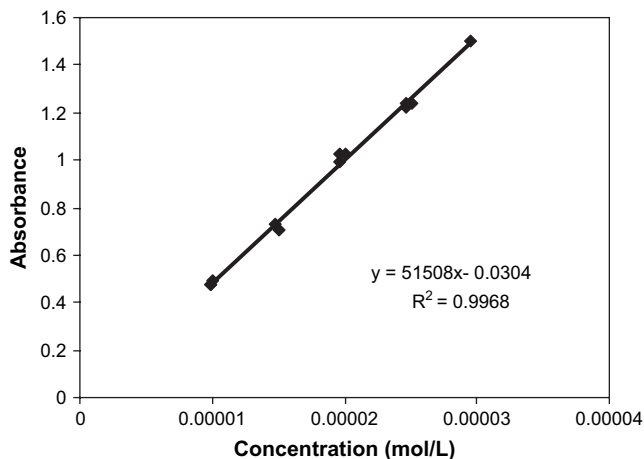


Fig. 6. Calibration curve used to develop the Beer's Law slope.

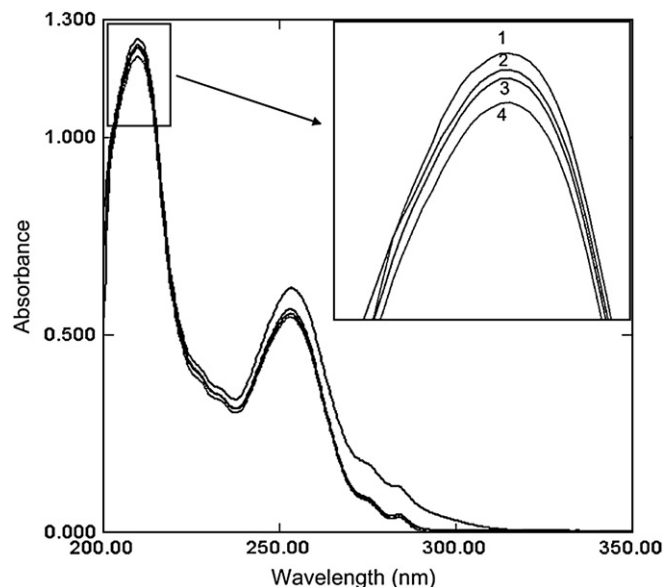


Fig. 7. Curves 1–3 show the effect drying times of 72, 48, and 24 h, respectively, have on the absorbance of SDCDPS samples. Curve 4 shows the effect that storage time in a desiccator for 15 days has on a sample that had been dried for 72 h prior to storage. (All samples were prepared at the same concentration.)

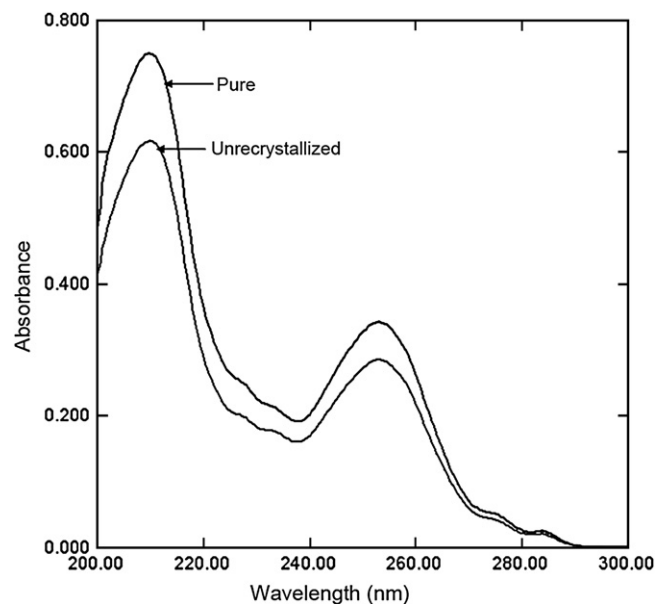


Fig. 8. Comparison of the absorbances of pure and unrecrystallized samples of SDCDPS.

solutions scaled with the concentrations linearly as shown in Fig. 5. These UV-vis absorbance data (peak at 210 nm) were used to develop the Beer's Law calibration curve (Fig. 6). The linear portion was plotted and the molar absorptivity ( $\epsilon$ ) was obtained from the slope of the straight line (Fig. 6). The Beer's Law plot for the SDCDPS monomer was expressed as the equation:  $A = 51508c - 0.0304$ .

Table 1  
Characterization of the model BPS copolymers

Copolymers	SDCDPS purity (%)	GPC results <sup>a</sup>			Degree of sulfonation by <sup>1</sup> H NMR (%)
		$M_n$ (kg mol <sup>-1</sup> )	$M_w$ (kg mol <sup>-1</sup> )	I.V. (dL g <sup>-1</sup> )	
BPS35	91.4	45.5	99.5	0.68	34.0
BPS40	91.4	57.0	82.2	0.64	39.4

<sup>a</sup> Viscosity detector, LiBr (0.05 M) NMP at 60 °C.



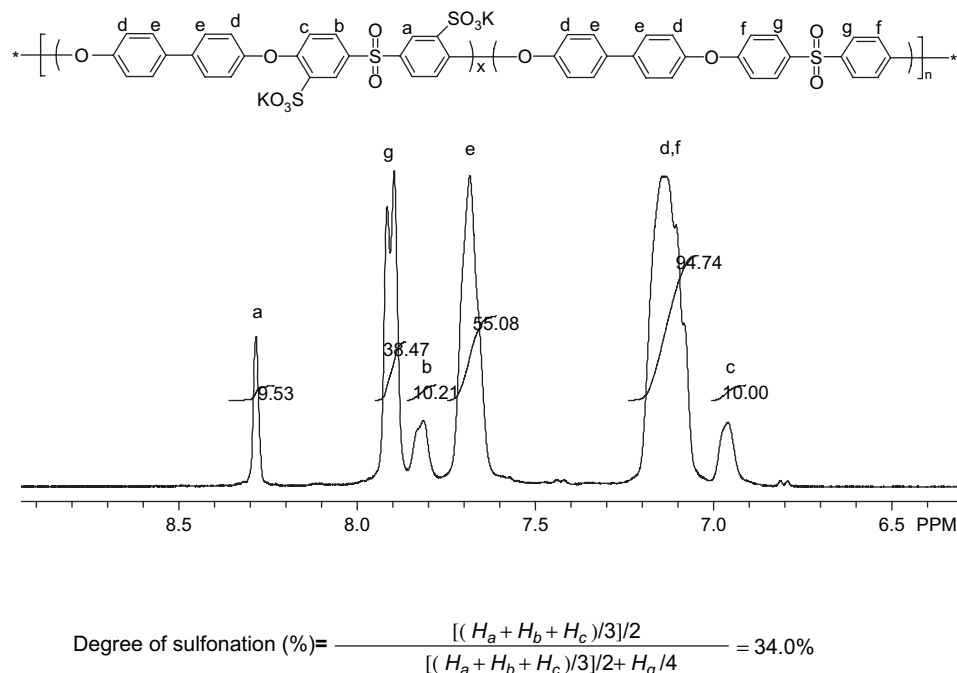


Fig. 9.  $^1\text{H}$  NMR of poly(arylene ether sulfone) copolymers (BPS35) was used to determine the degree of sulfonation [16].

Once this was established, the purity of the unrecrystallized monomer was determined by measuring the absorbance of a sample solution with a known concentration as described in Section 2.

Since SDCDPS is very susceptible to moisture uptake, the drying time and storage time were also studied. The recrystallized SDCDPS was first dried in a vacuum oven at  $160^\circ\text{C}$ , and the purity was measured after 24, 48, and 72 h of drying time. The purity was also measured after being stored in a desiccator for 15 days. (The sample had been previously dried for 72 h at  $160^\circ\text{C}$ .) It is shown in Fig. 7 that the SDCDPS needed to be dried for at least 48 h at  $160^\circ\text{C}$  to completely remove the water from the sample. Further, it can be inferred that SDCDPS must be dried immediately before copolymerization because it absorbed significant amounts of water after 15 days in a desiccator.

The purity of the unrecrystallized SDCDPS monomer, synthesized by Hydrosize Inc., was determined using the Beer's Law calibration curve. The unrecrystallized sample was used directly in copolymerization with DCDPS and BP. The absorbances of pure and unrecrystallized SDCDPS sample solutions prepared at the same concentration are compared in Fig. 8. It should be noted that because the sodium chloride salt may not be evenly distributed throughout the sample, thorough blending of the crude sample was very important in obtaining accurate results. The purity of the crude SDCDPS was calculated to be  $91.4\% \pm 0.5\%$ .

The model disulfonated poly(arylene ether sulfone) random copolymers (BPS) were characterized by GPC and intrinsic viscosity, in LiBr (0.05 M) modified NMP at  $60^\circ\text{C}$  (Table 1). The molecular weights for both polymers with 35 and 40 mol% degree of sulfonation exceeded  $45 \text{ kg mol}^{-1}$ , which allowed for tough films to be solution cast for PEM fuel cells [16]. The degree of sulfonation calculated from the  $^1\text{H}$  NMR spectra matched very well with the theoretical values (Fig. 9). These results confirmed that the UV-vis characterization method for determining the purity of crude or unrecrystallized SDCDPS is relatively accurate and applicable for direct copolymerizations.

#### 4. Conclusions

A novel characterization method for determining the purity of the disulfonated monomer, SDCDPS, has been developed using UV-

vis spectroscopy. Pure SDCDPS recrystallized from IPA/ $\text{H}_2\text{O}$  was used to establish a Beer's Law calibration curve, which was then used to determine the purity of the unrecrystallized product. The results also showed that the SDCDPS needed to be dried in a vacuum oven at  $160^\circ\text{C}$  for at least 48 h to completely remove the water. Since the SDCDPS absorbed small amounts of moisture after storage in a desiccator for several days, it is suggested to dry the SDCDPS directly before copolymerization. The model disulfonated poly(arylene ether sulfone) copolymers were synthesized by direct random copolymerization of the unrecrystallized SDCDPS with known purity, DCDPS, and BP. The relatively high molecular weights of the copolymers confirmed that this characterization method was applicable to accurately determine the purity and directly use the unrecrystallized SDCDPS, which eliminates the purification process. This is especially attractive for possible large scale production of the copolymers. It could also be utilized for the synthesis of block copolymers [21,23–26,28,29].

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