SYNTHESIS AND PURITY CHARACTERIZATION OF HIGH PURITY 3,3’-DISULFONATED-4,4’-DICHLORODIPHENYL SULFONE (SDCDPS) MONOMER BY ION CHROMATOGRAPHY

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By

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ABSTRACT

Proton exchange membrane (PEM) fuel cells demand monomers of high purity to produce membranes that are efficient and durable under a fuel cell’s severe conditions. One such monomer produced and tested is the disulfonated monomer, 3,3’-disulfonated-4,4’-dichlorodiphenyl sulfone (SDCDPS). SDCDPS is used in the production of high molecular weight disulfonated poly(arylene ether sulfone) block copolymers, and is therefore an excellent candidate for proton exchange membrane (PEM) fuel cells. Recrystallized SDCDPS purity has exceeded 99.5 %.

In this paper, we will explore how the purity of the recrystallized SDCDPS was characterized using $^1$H NMR spectroscopy coupled with Ion Chromatography. Copolymers synthesized from the recrystallized SDCDPS had greater molecular weights than the un-recrystallized material as confirmed by their high intrinsic viscosities, > 2.0 dL/g. These higher molecular weight copolymers allowed very tough films for PEMs to be solvent cast. This confirmed that the purity characterization method was relatively accurate and applicable.
DEDICATION

Dedicated to my dearest mother Retica, my loving wife Marcia and our children, Isaiah, Iyanna and Ian for their support, understanding and encouragement.
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PUBLICATIONS

Patents

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CHAPTER 1

INTRODUCTION

The recent surge in conventional fossil fuel prices has awakened great interest in finding an alternative affordable fuel. One promising green energy device is the proton exchange membrane fuel cells (PEMFC). The PEMFC are potentially one of the best candidates to replace conventional internal combustion engines in automobiles, stationary power and batteries in portable electronic devices because of high energy efficiency and environmental friendliness [1]. The interest here therefore, is the synthesis of potentially economical, commercially viable, and highly thermo-oxidatively stable engineering polymers as candidates for proton exchange membranes (PEMs) in fuel cells.

Various families of polymers with differing chemical structures and various strategies for incorporation of sulfonic acid groups were explored as PEM materials [2]. Sulfonated poly-(arylene ether sulfone)s, have generated great attraction for use in PEMs because of their well known oxidative and hydrolytic stability under a fuel cell’s harsh conditions [3]. Recent studies have shown that 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 [4]. Direct copolymerization method however, has its advantages over the post-modification method.
such as, its easy control of the position and degree of sulfonation, high acidity, and the ease of minimizing side reactions.

The monomer 3,3’-disulfonated-4,4’-dichlorodiphenyl sulfone (SDCDPS) is the monomer of interest for this study. SDCDPS was synthesized via electrophilic aromatic substitution with fuming sulfuric acid and later used in the direct copolymerization synthesis of proton exchange membranes for fuel cells. We modified the synthesis, purification and characterization procedure for 3,3’-disulfonated-4,4’-dichlorodiphenyl sulfone and 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 \([5,6]\). The modified synthesis, purification and characterization procedure for 3,3’-disulfonated-4,4’-dichlorodiphenyl sulfone monomer is the subject of this paper.

Knowing the purity of the disulfonated monomer is very important in obtaining high molecular weight copolymers using step-growth copolymerization as indicated in the Carothers equation (Figure 1). The impurities remaining in the SDCDPS monomer that reduces the formation of high molecular weight copolymers, if not considered during the monomer’s stoichiometric addition, are water and sodium chloride. These were used in excess to salt out the crude sulfonated monomer. Removal of the excess water is very effective with the use of a vacuum oven. Recrystallization of the dried crude monomer in high purity methanol has proven very effective in substantially reducing the sodium chloride impurity. This method of improving the disulfonated monomer’s purity eliminated the traditional approach involving two to three repeated recrystallizations of the crude disulfonated monomer with an alcohol/water system.
A novel method to characterize the purity of recrystallized SDCDPS using ion chromatography and proton NMR (\textsuperscript{1}H-NMR) spectroscopy was developed in this paper. The Bruker Avance 500 FT-NMR spectrometer with an operating field of 11.75 Tesla was used to characterize the SDCDPS monomer product by \textsuperscript{1}H-NMR (Figure 5) and a Dionex DX-500 Ion Chromatography instrument was used in the chloride analysis of the SDCDPS monomer. This paper provides an accurate and practical way to characterize the purity of SDCDPS by determining the quantitative presence of the chloride impurity from any residual sodium chloride that may be present. This information is of great importance to the production of PEM since the presence of the sodium chloride impurity inhibits the formation of high molecular weight membranes during the direct copolymerization synthesis of proton exchange membranes for fuel cells.

\[
M_w = \frac{M_o (1 + p)}{(1 - p)}
\]

\(M_o\) is the weight average molecular weight
\(M_o\) is the molecular weight of the repeating monomer unit
\(p\) is the extent of reaction

**Figure 1:** Carothers equation
CHAPTER 2

EXPERIMENTAL

2.1. Materials

High purity 4,4’-dichlorodiphenyl sulfone (DCDPS) monomer (Figure 4) from SLOSS Industries was purchase and used as received. Fuming sulfuric acid with 27–33 wt% of sulfur trioxide (SO₃) was purchased from PEEK Sulfur Incorporation and used as received. Sodium chloride pellets, 2 N sodium hydroxide and high purity methanol were purchase from Aldrich and used as received.

2.2. Synthesis

2.2.1. Synthesis of SDCDPS monomer

The synthesis of SDCDPS from DCDPS incorporated the synthetic procedure outlined previously [7, 8, 9, 10, 11]. A typical procedure proceeded as follows (Figure 2): DCDPS (287.0 g, 990 mmol) was dissolved in 600 mL of 30% fuming sulfuric acid (ca. 2-equiv excess) in a 1.0-L, three-necked flask equipped with an overhead mechanical stirrer and a argon inlet/outlet. The solution was heated to 110 °C for 6 h to produce a homogeneous solution. The light brown solution was then cooled to room temperature
and dissolved in 4.0 L of a 50/50 mixture of ice/water. 1.80 kg of sodium chloride pellets was added to the homogeneous mixture, producing a white precipitate identified as the disodium salt of SDCDPS monomer. The white precipitate was collected by and re-dissolved in 4.0 L of deionized water. The pH of this solution was then increased from a pH < 1 to a pH range of 6–7 by the addition of aqueous 2 N sodium hydroxide solution. An excess of NaCl (~1.80 kg) was added to salt out the SDCDPS monomer. The crude white SDCDPS monomer product was filtered and dried in a vacuum oven at 160 °C for 24 hours.

**Figure 2:** Synthetic scheme of crude SDCDPS monomer.

### 2.2.2. Purification of SDCDPS monomer

The purification of 3,3’-disulfonated-4,4’-dichlorodiphenyl sulfone monomer to remove sodium chloride was accomplished using a novel approach with high purity methanol. 900 mL of high purity methanol was heated to 60 °C and 180 g of the previously dried crude monomer was added to the heated methanol with vigorous
stirring. The mixture was thoroughly mixed for ninety seconds and vacuum filtered using a Buckner funnel using a Whatman #2 filter paper. The filtrate was refrigerated overnight producing fine white needlelike crystals over a twenty-four hour period. These SDCDPS hydrated monomer crystals were isolated by further filtration and transferred to a Pyrex dish. The Pyrex dish containing the hydrated white needlelike crystals was placed in a vacuum oven and dried under vacuum at 160 °C for at least 48 h to remove methanol and any water of hydration. At the end of the drying period, a fine white powder was recovered from the Pyrex dish and analytical tests were conducted on this material to determine whether or not it was the purified 3,3’-disulfonated-4,4’-dichlorodiphenyl sulfone monomer.

2.2.3. Synthesis of disulfonated poly(arylene ether sulfone) (BPS 35)
Disulfonated poly(arylene ether sulfone) copolymer was achieved with 35 mol % (BPS35) degree of disulfonation via direct copolymerization of SDCDPS, DCDPS, and 4,4-biphenol (BP) monomers (Figure 3). Three different disulfonated poly(arylene ether sulfone) model random copolymer (BPS35) syntheses were conducted. The first two syntheses utilized the crude SDCDPS monomer before recrystallization. In one of these synthesis, syntheses (A), the purity of the SDCDPS monomer was considered during the stoichiometric addition of the reagents however, in the second synthesis, synthesis (B), the purity of the SDCDPS monomer was not considered. The third synthesis, synthesis (C) utilized the recrystallized SDCDPS monomer to synthesize the disulfonated poly(arylene ether sulfone) model random copolymer (BPS35). The purity of the
SDCDPS monomer in each case, was determined by ion chromatography following the procedure described in Section 2.3.2.

The synthetic procedure reported is similar to the synthetic procedure reported previously [10, 11]. The DCDPS (25.866 g, 0.090 mol), SDCDPS (23.826 g, 0.049 mol), BP (25.804 g, 0.139 mol) monomers, and potassium carbonate (15% excess, 22.025 g) were transferred to a three-necked flask equipped with a mechanical stirrer, an argon inlet, and a Dean Stark trap. Dry N,N-dimethylacetamide (DMAc) (150 mL) was introduced to provide 35% (w/v) solid concentration, and the ratio of DMAc to toluene (v/v), an azeotroping agent, was 2 : 1. The reaction mixture was refluxed for 6 h at 145°C to complete the dehydration process. The reaction temperature was slowly increased to 180°C for 36 h, after gradual removal of the toluene. The viscous reaction product was cooled and diluted with DMAc (100 mL) and precipitated in deionized water (1-L) 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.
Figure 3: Synthetic scheme for 35 mol\% (BPS 35) disulfonated poly(arylene ether sulfone) random copolymer

2.3. Characterization

2.3.1. Characterization of SDCDPS monomer

The SDCDPS monomer chemical structure was confirmed by proton nuclear magnetic resonance ($^1$H NMR) spectroscopy using a Bruker Avance 500 FT-NMR spectrometer with an operating field of 11.75 Tesla (Figure 4). The purity of the SDCDPS monomer with respect to the sodium chloride content was determined by ion chromatography using a Dionex DX-500 Ion Chromatography instrument (Fig. 4). Proton nuclear magnetic resonance ($^1$H NMR) analyses were conducted with the Bruker Avance 500 FT-NMR spectrometer to confirm the chemical structure of the SDCDPS monomer. Spectra were obtained using dried sodium acetate (NaAc) as the reference material and deuterium oxide (D$_2$O) as the solvent. These spectra were consistent with the spectrum displayed in Figure 5. The split peak incorporated at about 8.38 ppm and integration values confirm disulfonation. There are also notable differences between the
$^1$H NMR spectrum of DCDPS predicted in D$_2$O solvent (Figure 4) and the $^1$H NMR spectrum of recrystallized SDCDPS monomer in D$_2$O solvent (Figure 5).

**Figure 4:** $^1$H NMR spectrum of DCDPS observed in D$_2$O solvent.
2.3.2. Procedure for SDCDPS monomer purity characterization by Ion Chromatography.

Purity characterization of the SDCDPS monomer was determined using a Dionex DX-500 Ion Chromatography instrument. The only impurity in the recrystallized SDCDPS monomer is the excess sodium chloride used during the SDCDPS monomer synthesis. The purity of the SDCDPS monomer was determined by doing a chloride analysis on samples of the monomer. The procedure was as follows: the instrument is equilibrated overnight before any analysis is started. A low-level chloride standard was injected to verify detection limits, signal to noise ratios, and retention times of any analytes. Next, a water blank is injected to verify the cleanliness of the system and assure no residual chloride is present. A 5-point calibration curve is injected and verified with an initial calibration verification injection of the L3 standard. Samples are then injected
and a closing calibration verification is injected at the end of the sequence. Integration and calculation of the chloride peak reveals 0.46% sodium chloride in the recrystallized SDCDPS monomer and 8.76% an unrecrystallized monomer sample.

**Figure 6:** IC chromatogram of the recrystallized SDCDPS monomer.

<table>
<thead>
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<th>Samples from different SDCDPS monomers</th>
<th>SDCDPS % Chloride content</th>
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<tr>
<td></td>
<td>Recrystallized</td>
</tr>
<tr>
<td>A</td>
<td>0.382</td>
</tr>
<tr>
<td>B</td>
<td>0.287</td>
</tr>
<tr>
<td>C</td>
<td>0.577</td>
</tr>
<tr>
<td>D</td>
<td>0.463</td>
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Table 1: SDCDPS % chloride content before and after recrystallization
2.3.3. Characterization of disulfonated poly(arylene ether sulfone) (BPS 35)

One quick way to determine whether or not high molecular weight disulfonated poly(arylene ether sulfone) (BPS 35) product was produced at the completion of the synthesis is to determine the BPS 35 product intrinsic viscosity ($\eta$). A low molecular weight disulfonated poly(arylene ether sulfone) (BPS 35) product is considered if the intrinsic viscosity is less than 0.7 dL/g and is undesirable because it produces poor proton exchange membranes (PEM) for fuel cells. A high molecular weight disulfonated poly(arylene ether sulfone) (BPS 35) product is considered to have an intrinsic viscosity greater than 1.0 dL/g and is desirable for producing PEMs for fuel cells.

One must recall the intrinsic viscosity is a measure of the hydrodynamic volume/mass of the polymer in a solvent. The sulfonated poly (arylene ether sulfone) copolymers have an increasing number of pendent bulky sulfonic acid moieties as the molar amount of the sulfonated dihalide is increased. The bulky side groups make the copolymer appear larger and contribute to the observed high intrinsic viscosities. Similar trends of increased intrinsic viscosities with increased ionic content have been reported by several researchers for a number of polymer systems [12, 13, 14]. Table 2 displays the intrinsic viscosities of the copolymers synthesized.
<table>
<thead>
<tr>
<th>BPS 35 Copolymers</th>
<th>$[\eta]^{\text{NMP,25oC}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (used crude SDCDPS of known purity)</td>
<td>1.1</td>
</tr>
<tr>
<td>B (used crude SDCDPS of unknown purity)</td>
<td>0.4</td>
</tr>
<tr>
<td>C (used recrystallized SDCDPS of known purity)</td>
<td>1.2</td>
</tr>
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</table>

**Table 2:** Intrinsic viscosity values of various Poly(arylene ether sulfone) Sulfonated Copolymers with copolymerization temperature of 180°C.
CHAPTER 3

RESULTS AND DISCUSSION

High purity SDCDPS monomer was prepared via electrophilic aromatic substitution on DCDPS monomer in fuming sulfuric acid with 27–33 wt% of sulfur trioxide (SO$_3$). The reaction conditions for the crude SDCDPS monomer synthesis are outlined in Figure 2. Results from $^1$H NMR spectroscopy of the crude SDCDPS monomer did not indicate any monosulfonated byproduct or residual starting DCDPS monomer impurities. However, because sodium chloride was used in excess to salt out the SDCDPS from the product solution, it was the only impurity present in the product.

This crude SDCDPS monomer was then purified following the purification procedure outlined in section 2.2.2 of this paper. Results from $^1$H NMR spectroscopy of the recrystallized SDCDPS monomer in D$_2$O solvent indicate the formation of the disulfonated SDCDPS monomer product from the synthesis reaction. Results from the ion chromatography chloride analysis for determining the percentage of sodium chloride impurity indicate a sodium chloride impurity less than 0.5%. These results confirm high purity SDCDPS monomer production with SDCDPS monomer purity greater than 99.5%.

Study has shown that the impurity sodium chloride has a negative influence on the nucleophilic step-growth copolymerization reaction that will produce membranes that are efficient and durable under a fuel cell’s severe conditions. It is therefore necessary to
accurately determine the purity of the SDCDPS disulfonated monomer and most desirable to use high purity recrystallized SDCDPS monomer during the nucleophilic step-growth copolymerization reaction to reduce the sodium chloride impurity negative impact on producing membranes that are efficient and durable under a fuel cell’s severe conditions.

The $^1$H NMR spectrum in Figure 5 of the recrystallized SDCDPS monomer did not indicate any monosulfonated byproduct or residual starting DCDPS monomer impurities. The presence of a monosulfonated by product will typically be seen on the $^1$H NMR spectrum at a chemical shift to the left of the 8.38 – 8.39 ppm disulfonated peaks. Clearly, no peaks were observed in this area of the spectrum indicating the absence of any monosulfonated byproduct impurities. Also, any residual DCDPS monomer, Ha’, will have a chemical shift slightly to the left of the 7.7 ppm SDCDPS monomer peaks Ha. Clearly, no peaks were observed in this area of the spectrum indicating the absence of any residual starting DCDPS monomer impurities. Integrated values from the $^1$H NMR spectrum in Figure 5 of the recrystallized SDCDPS monomer confirms disulfonation. The purity of the sodium acetate standard must be carefully determined because it will affect the analytical results from the $^1$H NMR spectroscopy. The characterization of the SDCDPS monomer via $^1$H NMR spectroscopy was done in triplicates to confirm the integration of the spectra analytical results. Having characterized the SDCDPS monomer it’s purity was easily be determined from the $^1$H NMR spectroscopy results, however, it was necessary to confirm these results by using ion chromatography to determine the chloride content in the product and hence the amount of sodium chloride impurity present.
The purity characterization of the SDCDPS monomer was determined using a Dionex DX-500 Ion Chromatography instrument. The procedure used to determine the chloride content and ultimately the sodium chloride percent in the SDCDPS monomer sample is outlined in section 2.3.2 of this paper. The Dionex DX-500 Ion Chromatography instrument conditions included an IonPac AS-11 Analytical (4 x 250mm) column, KOH eluent cartridge, thirty-five minutes variable time interval program with varied molar concentration of KOH, sample injection of 10 µL and a flow rate of 2.0 mL/min. The samples were run in triplicate and the chromatographs, Figure 6, were in integrated to determine the percent of chloride in the SDCDPS monomer sample. These integrated values were then used to calculate the sodium chloride percent in the SDCDPS monomer. The purity calculated from the $^1$H NMR spectra matched very well with the IC results of less than 0.5% sodium chloride present in the SDCDPS recrystallized monomer. These results confirmed that the $^1$H NMR spectra characterization method and the IC purification method for determining the purity of crude or unrecrystallized SDCDPS are relatively accurate. This high purity SDCDPS monomer can now be used in the nucleophilic step-growth copolymerization reaction that will produce membranes that are efficient and durable under a PEM fuel cell’s severe conditions.
CHAPTER 4

CONCLUSIONS

Synthesis and purity characterization methods of recrystallized SDCDPS monomer for use in the nucleophilic step-growth copolymerization reaction that will produce membranes that are efficient and durable under a PEM fuel cell’s severe conditions were developed using ion chromatography. Crude SDCDPS and pure SDCDPS recrystallized from methanol were used to investigate the influence of sodium chloride on nucleophilic step-growth copolymerization reactions. $^1$H NMR spectroscopy gave an estimation of the purity of the recrystallized SDCDPS monomer while a novel ion chromatography approach was used to determine the percentage of the sodium chloride. The results showed that the SDCDPS monomer contained less than 0.5 % sodium chloride, a very important piece of information needed for later use of the SDCDPS monomer. The synthesis of disulfonated poly(arylene ether sulfone) copolymers were synthesized by direct random copolymerization of the recrystallized SDCDPS with known purity as determined by ion chromatography and $^1$H NMR. The use of this recrystallized SDCDPS monomer gave rise to relatively high molecular weights copolymers confirming that this characterization method was applicable to accurately determine the purity of the SDCDPS monomer.
LIST OF REFERENCES


