

A Functional Monomer to Synthesize Sulfonated Poly(ether ether ketone) with Sulfonic Acid Group in the Pendant Side Chain

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ABSTRACT: A functional monomer which enables the synthesis of sulfonated poly(ether ether ketone) (SPEEK) polymer with the sulfonic acid group in the pendant side chain has been successfully developed. 1, 3-propane sultone was used as the model compound to introduce the side chain moiety in the monomer. The above sulfonated monomer (0.50 mol) along with 4, 4'-difluorobenzophenone (0.50 mol) were reacted with bisphenol-A (1.0 mol) to obtain the SPEEK polymer with the sulfonic acid

group in the pendant side chain. All the intermediates and the SPEEK polymer were characterized using $^1\text{H-NMR}$. The SPEEK polymer is expected to have improved mechanical and electrical properties for PEM fuel cell application. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 3331–3336, 2012

Key words: fuel cells; polymer electrolyte; SPEEK; sulfonic acid; pendant side chain; 1, 3-propane sultone

INTRODUCTION

Polymer electrolyte membrane (PEM) fuel cells are considered as pollution-free, quiet, and green power generation devices for various applications ranging from mobile phones to automobile traction.^{1,2} After years of persistent research efforts, PEM fuel cell technology has entered the commercial phase and PEM fuel cells are now available in the market. PEM fuel cells still need to overcome challenges such as high manufacturing cost and limited durability to become cost competitive with conventional power generation technologies. The polymer electrolyte membrane is a key component of PEM fuel cells. Perfluorosulfonic acid polymer is commonly used as the membrane material in PEM fuel cells (for example, DuPont's Nafion). Although Nafion performs well at temperatures below 70°C, its glass transition temperature is around 110°C. Because of the low glass transition temperature, the polymer exhibits membrane dry-out, reduced proton conductivity, and poor fuel cell performance above 80°C. Nafion is also expensive and must undergo hazardous manufacturing processes.

To overcome the limitations of the Nafion membrane, aromatic hydrocarbon polymers such as poly

(ether ether ketone),³ polybenzimidazole,⁴ poly(arylene ether sulfone),⁵ polyimide,⁶ etc. are actively being studied. Of the many classes of polymers, poly(ether ether ketone), or PEEK, is being extensively investigated due to its outstanding mechanical, thermal and chemical properties.⁷ PEEK can be converted into proton-conducting poly(ether ether ketone), or SPEEK, by reacting it with concentrated sulfuric acid (H_2SO_4) as it easily undergoes an electrophilic substitution reaction on the aromatic ring. However, the SPEEK polymer with a high degree of sulfonation (DS) swells excessively at elevated temperatures due to higher water-uptake causing mechanical disintegration; which is due to the random distribution of sulfonic acid groups along the polymer back-bone as the sulfonation of PEEK with sulfuric acid (H_2SO_4) is heterogeneous in nature.⁸ Moreover, the harsh environment during the sulfonation process may degrade the polymer. To control DS, SPEEK polymers have been synthesized using sulfonated monomers where precise control of DS is possible.⁹

SPEEK polymers prepared from sulfonated monomers are reported to have comparable water swelling, proton conductivity, and thermal stability, but significantly improved methanol diffusion coefficient when compared with postsulfonated SPEEK.¹⁰ An ideal PEM fuel cell membrane should have distinct microphase separation between the hydrophobic and hydrophilic segments in which the hydrophilic sulfonic-acid groups form the proton-conducting channels, and the hydrophobic polymer backbone provides mechanical stability to the membrane. Since

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the sulfonic acid groups in the SPEEK matrix are present as a part of the polymer backbone, this rigid polyaromatic backbone prevents continuous ionic clustering from occurring; the resulting morphology is not ideal for effective microphase separation. Therefore, the proton-conducting channels of SPEEK are narrow when compared with that of Nafion.¹¹

Considering the above issues, an effective way to balance the mechanical properties and proton conductivity of SPEEK is to redirect the sulfonic acid groups away from the polymer backbone similar to Nafion. In such morphology, cohesion between the hydrophobic polymer backbone will be retained even in the presence of the highly swollen hydrophilic phase. Recently, hydrocarbon polymers with the sulfonic acid group in a pendant side chain have been reported by many research groups.^{12–15} Karlsson et al.¹² prepared sulfonated polysulfone with the sulfonic acid group in a pendant side chain, but the process involved complex reaction scheme of reacting with metallic lithium at -40°C . Lafitte et al.¹³ introduced the sulfonic acid group in a side chain by following a postsulfonation technique; the process again involves reacting with butyllithium at -78°C . They reported that the resulting membranes exhibited low water uptake, low swelling ratios as well as appropriate conductivity. Yoshima and Iwasaki¹⁵ have successfully synthesized and characterized a poly(ether sulfone) polymer with perfluoroalkyl sulfonic acid groups in the pendant side chain. The polymer had a higher α -relaxation temperature than Nafion and a higher breaking elongation than sulfonated poly(ether sulfone) which are desirable for high-temperature operation and stress tolerance in the fuel cell. The membrane gave an impressive fuel cell performance of $800\text{ mW}/\text{cm}^2$ comparable to Nafion-112 membrane.

However, simple synthetic methods for the preparation of SPEEK polymers with the sulfonic acid group in the pendant side chain are not available. In this work, a novel functional monomer has been developed to synthesize a SPEEK polymer with the sulfonic acid group in the pendant side chain. Preliminary studies of the synthesis and characterization of the functional monomer, intermediates and the SPEEK polymer are presented in this communication.

SYNTHESIS

Chemicals

4-Fluorophenol, 4-fluorobenzoyl chloride, triethylamine (TEA), aluminum chloride (AlCl_3), diethyl ether, 2-propanol, bisphenol-A, dimethyl acetamide (DMAc), potassium carbonate (K_2CO_3), silica gel, petroleum ether, chloroform, acetone, sodium hydroxide (NaOH), toluene, hydrochloric acid (HCl),

sodium hydride (NaH), 1,3-propane sultone, tetrahydrofuran (THF) and methanol (MeOH) all from Sigma Aldrich, USA were used as received without further purification.

Synthetic steps

Synthetic steps 1-4 are shown in Scheme 1. Each step is described below.

Synthesis of 4, 4'-difluorophenyl benzoate

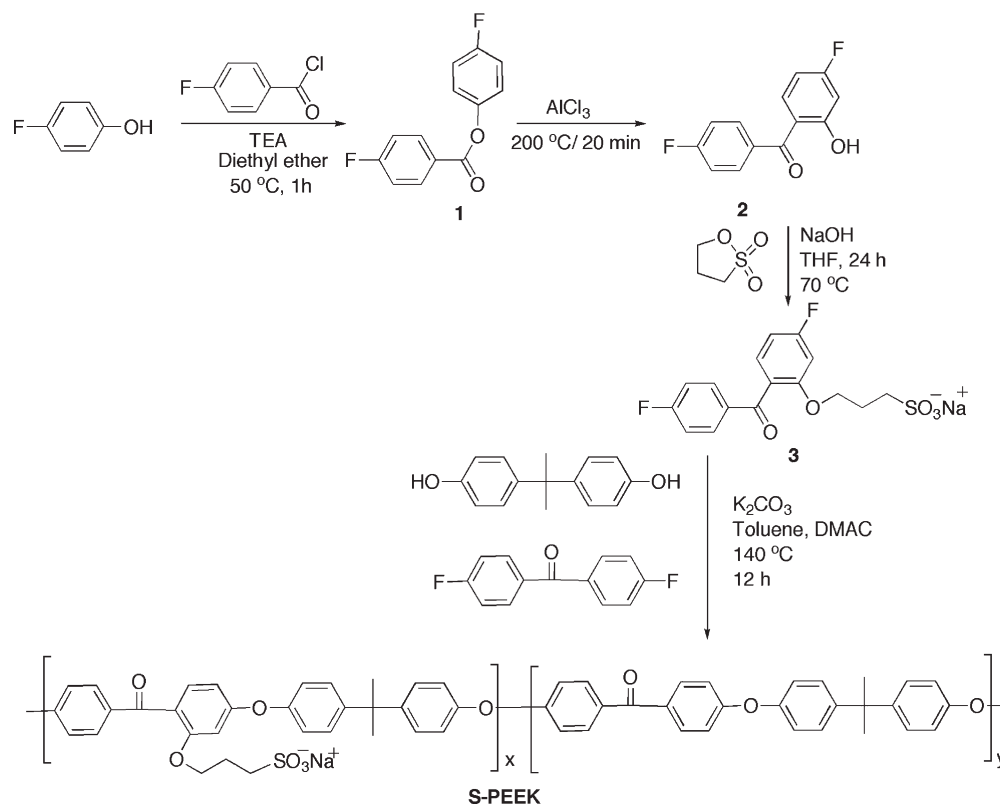
Initially, 100 mL of diethyl ether was transferred into a 500-mL round-bottomed flask. Then, 5.0 g (0.0446 mol) of 4-fluorophenol was dissolved and 4.5 g (0.0446 mol) of TEA was added. Next, 7.7 g (0.0446 mol) of 4-fluorobenzoyl chloride was slowly added at 50°C under nitrogen (N_2) atmosphere and the mass was maintained at the same temperature for 1.0 h under constant stirring. Then, 20.0 g of 10 wt % NaOH solution was slowly added to dissolve the triethylamine hydrochloride (TEAHCl). The organic phase was dried, evaporated, and the residue was recrystallized in petroleum ether to get pure crystals of 4, 4'-difluorophenyl benzoate (yield 85%). The compound was characterized using $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ , ppm): 7.04 (m, 2H), 7.09 (m, 2H), 8.12 (q, 4H).

Synthesis of (4-fluoro-2-hydroxyphenyl)-4-fluorophenyl methanone

3.8 g (0.016 mol) of 4, 4'-difluorophenyl benzoate was mixed with 2.59 g (0.019 mol) of AlCl_3 under N_2 atmosphere and heated to 200°C over a heating mantle for 20 min. It was cooled, and the hard solid lump was ground to a fine powder and slowly added to ice-cooled 10% HCl solution under stirring. The product was extracted using diethyl ether, dried free of moisture, evaporated, and crystallized in petroleum ether to get the crystalline (4-fluoro-2-hydroxyphenyl)-4-fluorophenyl methanone (yield 75%). The product was characterized using $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ , ppm): 6.96 (m, 1H), 7.15 (m, 4H), 7.65 (m, 2H), 11.50 (s, 1H).

Synthesis of 4-fluorophenyl-4-[fluoro-2-(3-sulfonyl propoxy)] phenyl methanone

In this step, 3 g (0.0128 mol) of (4-fluoro-2-hydroxyphenyl)-4-fluorophenyl methanone was dissolved in 50 mL of THF. Then, 1.02 g of 60 wt % NaH was slowly added under N_2 atmosphere and 1.25 g of 1, 3-propane sultone was added and maintained at 70°C for 24 h under stirring. The mass was cooled to room temperature, 5 g of MeOH was slowly added to destroy the unreacted NaH if present, the solvent was allowed to evaporate, and the product was then



Scheme 1 Reaction scheme.

purified on a silica gel column using chloroform + acetone mixture as eluants. The product, 4-fluorophenyl-4-[fluoro-2-(3-sulfonyl propoxy)] phenyl methanone was isolated in 60% yield and characterized using ¹H-NMR (400 MHz, D₂O, δ , ppm): 1.67 (m, 2H), 2.19 (t, 2H), 3.74 (t, 2H), 6.81 (m, 2H), 6.98 (m, 3H), 7.48 (m, 2H).

Synthesis of SPEEK polymer with the sulfonic acid group in the pendant side chain

SPEEK with the sulfonic acid group in the pendant side chain was synthesized using the sulfonated monomer as prepared above (0.5 mol), 4, 4'-difluorobenzophenone (0.50 mol) and bisphenol-A (1.0 mol) using K₂CO₃ (1.25 mol) as the base in DMAC. The monomers were charged along with DMAC, toluene, and K₂CO₃ under N₂ atmosphere. The water formed in the reaction was removed using a Dean and Stark apparatus at 110°C. The reaction mass was refluxed for 5.0 h and then toluene was distilled out and the temperature was increased to 140°C. The polymerization was continued at 140°C for 12 h. Then the polymer was precipitated out by pouring into ethanol + water mixture. It was repeatedly washed with water to remove the inorganic salts and dried at 80°C in a vacuum oven (yield 80–90%). The polymer was characterized using ¹H-NMR (400 MHz, DMSO-d₆, δ , ppm): 1.63–.79 (m, 12H), 1.79 (m, 2H), 2.31

(m, 2H), 4.04 (m, 2H), 6.71 (m, 1H), 7.02–7.11 (m, 12H), 7.13–7.28 (m, 4H), 7.30–7.40 (m, 8H), 7.71–7.83 (m, 6H).

Molecular weight of the polymer was determined by gel permeation chromatography (GPC) using Styragel HR1 column on Waters (USA) Breeze GPC system. THF at the rate of 1 mL/min was used as the mobile phase. About 2 wt % solution of SPEEK polymer in THF was used for the analysis. Polystyrene samples of different molecular weight were used to generate the calibration curve.

RESULTS AND DISCUSSION

Poor solubility of the PEEK polymers in many of the solvents is a major hindrance for the introduction of side chain functionalities in the PEEK polymer backbone. Our goal was to develop monomers with the sulfonic acid group attached in the pendant side chain so that the sulfonated monomers could be used to prepare SPEEK polymers with sulfonic acid group in the pendant side chain. The PEEK polymers are normally synthesized by the aromatic nucleophilic substitution of bisphenols with halogen substituted aromatic ketones such as 4, 4'-difluorobenzophenone. We were interested in introducing a suitable functional group in the 4, 4'-difluorobenzophenone which would enable the synthesis of a SPEEK polymer with the sulfonic acid group in the

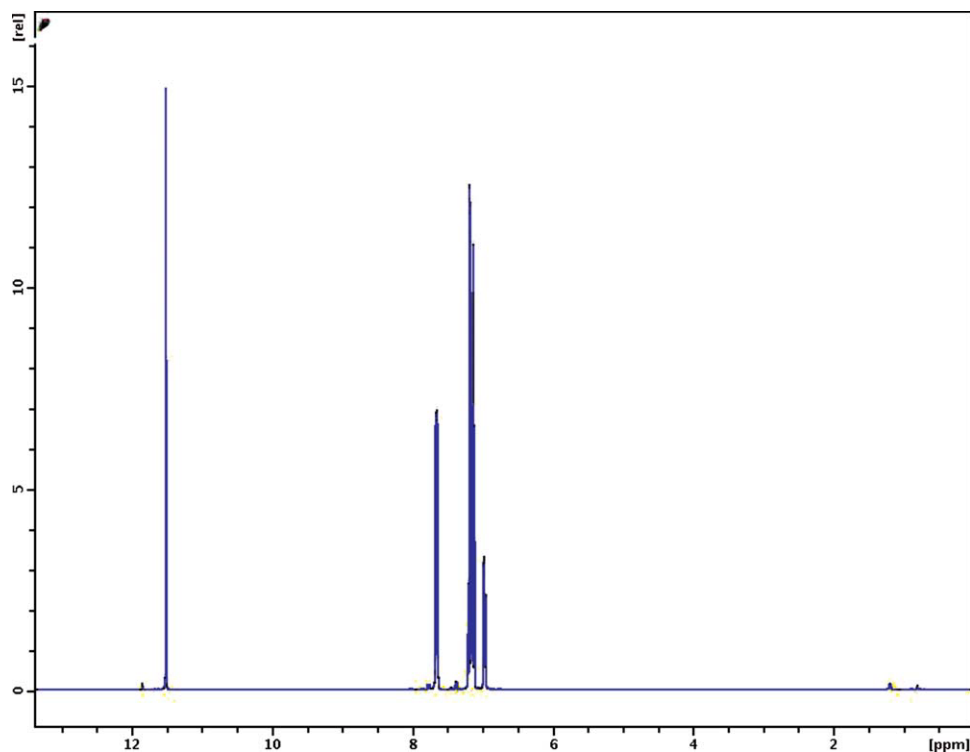


Figure 1 ^1H NMR spectrum of (4-fluoro-2-hydroxyphenyl)-4-fluorophenyl methanone. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

pendant side chain. All the synthetic steps developed in this study are shown in Scheme 1. Krause et al.¹⁶ have reported that the phenolic esters when heated with aluminum chloride at 200°C undergo Fries rearrangement to give hydroxyl ketones. We exploited this reaction to introduce the hydroxyl functional group in the 4, 4'-difluorobenzophenone molecule. The hydroxyl group was successfully introduced in 4, 4'-difluorobenzophenone as per the procedure discussed in Step 2 of the synthetic procedure. The ^1H -NMR spectrum of hydroxyl substituted 4, 4'-difluorobenzophenone is given in Figure 1. The singlet peak at 11.50 ppm confirms the presence of hydroxyl group in the molecule.

The pendant sulfonic acid group could be easily attached to the 4, 4'-difluorobenzophenone via the hydroxyl functional group. It has been reported in the literature that the sultones undergo ring opening substitution with the hydroxyl groups in the presence of a base like sodium hydride.^{17–19} The Step 2 product undergoes quantitative salt formation when reacted with NaH which confirms the presence of -OH group in the molecule. We have demonstrated the scheme using 1,3-propane sultone as the model compound. The pendant sulfonic acid substituted monomer was isolated in pure form using column chromatography. Polymerization of pendant sulfonic acid group substituted monomer as synthesized in step 3 (0.50 mol), 4, 4'-difluorobenzophenone

(0.50 mol) and Bisphenol-A (1.0 mol) was carried out as per the polymerization procedure described in Step 4. The SPEEK polymers with the sulfonic acid group in the pendant side chain were obtained in 80–90% yield. The ^1H -NMR spectrum of the synthesized SPEEK polymer with the sulfonic acid group in the pendant side chain is shown in Figure 2. The ^1H -NMR peaks in the range of 1.63–1.79 ppm are due to the presence of $-\text{CH}_3$ groups of bisphenol-A; peaks at 1.79, 2.31, and 4.04 ppm correspond to the three $-\text{CH}_2-$ groups in the pendant side chain. The ^1H -NMR signals in the range of 6.5–8.0 ppm are due to the aromatic protons in the SPEEK polymer. Hence, the ^1H -NMR spectrum nicely confirms the synthesis of the SPEEK polymer with the sulfonic acid group in the pendant side chain. The above discussed scheme has demonstrated a new, simple synthetic method for the synthesis of SPEEK polymer with the sulfonic acid group in the pendant side chain.

The synthesized SPEEK polymers totally dissolved in solvents like DMSO, DMF and form a nice continuous transparent film. However, the films got disintegrated on pouring into water which is mainly due to low molecular weight of the obtained polymers. To get an idea about the molecular weight of the obtained polymers, gel permeation chromatography analysis was carried out as per the conditions discussed above. The GPC trace of the synthesized SPEEK polymer is given in Figure 3. The GPC trace

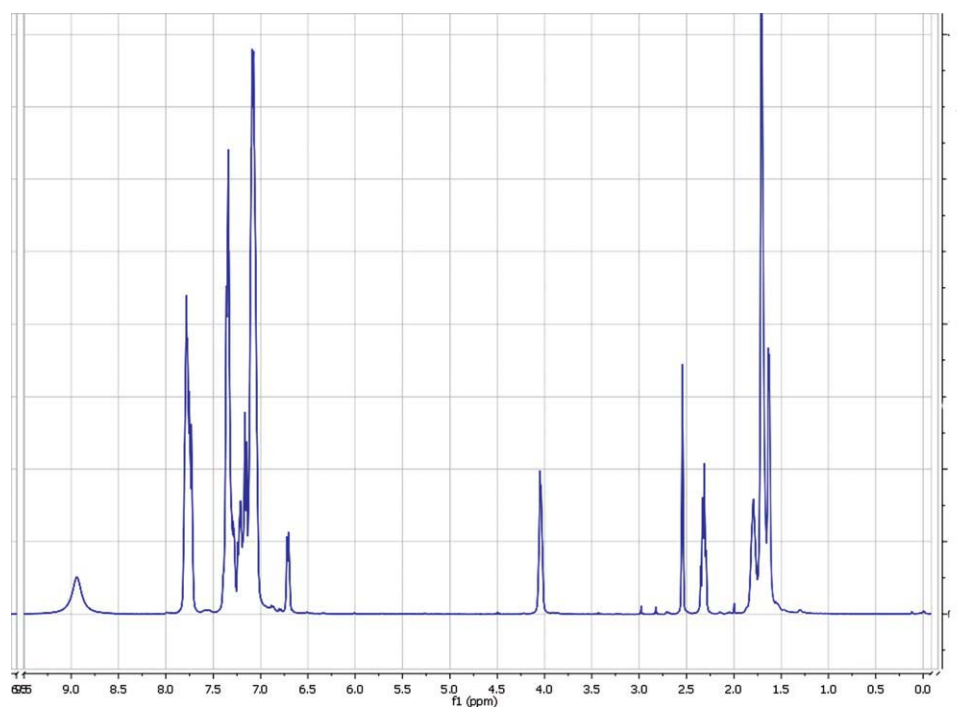


Figure 2 ¹H-NMR spectrum of synthesized SPEEK polymer in DMSO. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

shows one major peak and three minor peaks, which indicates the presence of oligomers with different molecular weights. On the basis of the calibration curve, a molecular weight of 4873 was calculated for the major GPC peak. Further studies like membrane formation and characterizations etc., could not be carried out due to the low molecular weight of the obtained polymers. We could observe precipitation of the polymer during the polymerization process which could be the main reason for the low molecular weight of the obtained polymers. We have successfully developed a simple synthetic scheme to synthesize SPEEK polymer with sulfonic acid group

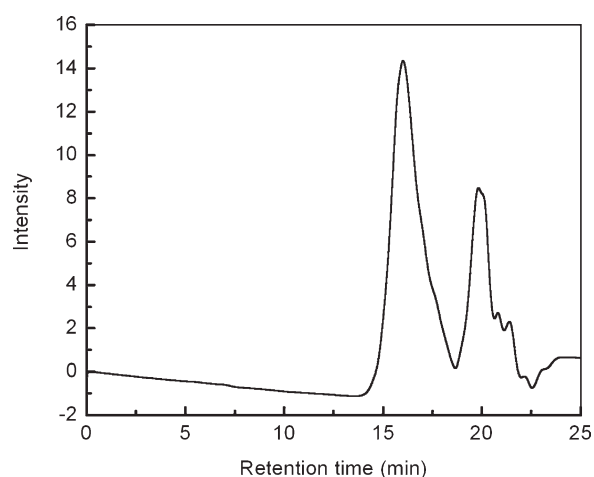


Figure 3 GPC chromatogram of synthesized SPEEK polymer.

in the pendant side chain. Even though, all the intermediates and the final polymer were isolated in pure form, the SPEEK polymer with the sufficiently high molecular weight could not be obtained in this study. This was mainly due to the precipitation of the oligomers during the polymerization. The polymerization process needs detailed further study to avoid the precipitation and to get a polymer with sufficiently high molecular weight.

CONCLUSIONS

A hydroxyl functional group substituted 4, 4'-difluorobenzophenone monomer was prepared by the simple Fries rearrangement of the phenolic ester. The SPEEK polymer with the sulfonic acid group in the pendant side chain was successfully prepared by attaching the pendant side chain via the hydroxyl group in the functional monomer. The simple synthetic scheme developed in this work could enable the synthesis of SPEEK polymers with controlled swelling and improved electrical properties for PEM fuel cell applications.

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