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Functionalized Sulfone and Sulfonamide Based Poly(arylene ether)s

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FUNCTIONALIZED SULFONE AND SULFONAMIDE BASED POLY(ARYLENE ETHER)S

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science

By:

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2014
Wright State University

WRIGHT STATE UNIVERSITY
GRADUATE SCHOOL

May 27, 2014

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Marina Andrejevic ENTITLED Functionalized Sulfone and Sulfonamide Based Poly(arylene ether)s BE ACCEPTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF Master of Science.

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ABSTRACT

Marina Andrejevic M.S., Department of Chemistry, Wright State University, 2014.
Functionalized Sulfone and Sulfonamide Based Poly(arylene ether)s

A series of fluorinated poly(arylene ether)s, PAE, bearing sulfonated pendent sulfonyl groups, was prepared. A range of Ion Exchange Capacity (IEC) values were achieved by varying the ratios of sulfonated and non sulfonated monomers. Incorporation of both of the monomers was confirmed by NMR spectroscopy and characterization of the thermal properties was done using thermogravimetric analysis (TGA) and differential scanning (DSC). Polymers with these IEC values were synthesized in order to explore their use as a potential alternatives to the widely studied proton exchange membrane, Nafion®, with an IEC of 0.91 meq/g.

Using *N*-phenyl-3,5-difluorobenzene sulfonamide as the starting material a series of *N*-alkyl derivatives, with chain lengths of 3 to 12 carbon atoms, was prepared and characterized followed by conversion to the corresponding PAE. The polymer structure was confirmed by ^{1}H and ^{13}C NMR spectroscopy. Molecular weight data were obtained by size exclusion chromatography (SEC) and thermal data were acquired using TGA and DSC. The effect of alkyl chain length on the thermal stability and glass transition temperatures, T_g, values was determined. Increasing the alkyl chain length led to a decrease in the T_g values, which ranged from 111 down to 46 °C.

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DEDICATION

I would like to dedicate this thesis to my parents, Branko and Lijana Andrejevic. Thank you for sacrificing so much of your own lives to give me opportunity to obtain a higher education. Words cannot express my gratitude for your unconditional love and support you’ve given me through the years.

1. INTRODUCTION

1.1. Polymer Thermal Transitions

There are three major polymer thermal transition temperatures: glass transition temperature (T_g), crystallization temperature (T_c) and melting temperature (T_m). The glass transition temperature is the temperature at which amorphous polymers (or portions of a polymer) undergo a transition (soften) from solid (glassy state) to rubber or viscous liquid. The melting temperature is the temperature at which ordered crystalline regions of polymer melt. The crystallization temperature is the temperature at which polymer crystallizes from melt upon cooling forming ordered crystalline regions (or crystallize upon heating above T_g). All three factors are of great importance because they affect polymer properties and define the temperature limits for processing and numerous polymer applications. [1]

There are two different morphologies that polymers can adopt: disordered amorphous regions and highly ordered crystalline regions. The extent to which polymers crystallize depends on high structural regularity and intermolecular forces between polymer chains. The inability of polymer chains to fully disentangle and line up, upon cooling, typically prevents them from being fully crystalline. When crystalline regions are interconnected with amorphous regions the polymer forms what is called the Fringed micelle model.

Unlike melting, which is a first order transition, linear, fully amorphous polymers undergo a second order transition as they acquire enough energy for their chains to start rotating around sigma bonds, known as the glass to rubber transition. There are five regions observed in a typical amorphous polymer: glassy state, leathery region, rubbery plateau, rubbery and viscous region (Figure 1).[2]

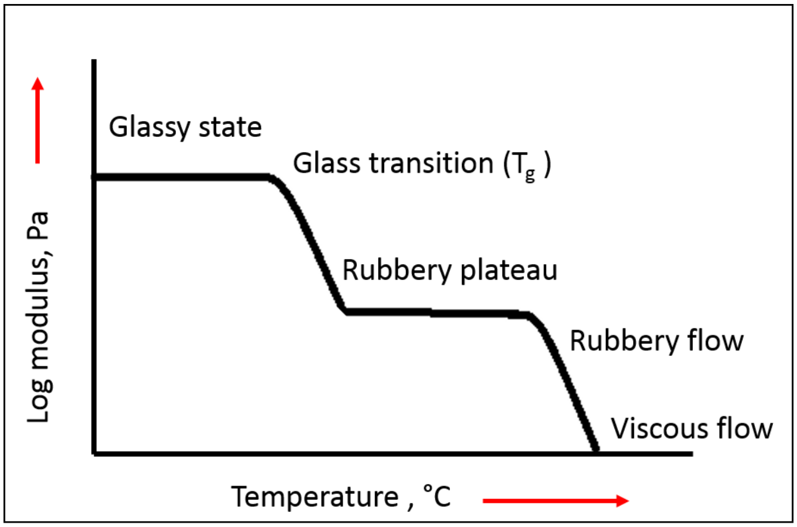

Figure 1. Glass to rubber transition of an amorphous polymer.

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Polymer moduli change greatly in these regions from brittle and glassy with little or no translational motions to leathery, highly elastic and in the end rubbery and viscous liquid. There are various techniques that can be utilized to measure thermal transitions such as: differential scanning calorimetry (DSC), thermomechanical analysis (TMA) and dynamic mechanical analysis (DMA). The first two techniques are based upon polymer changes as a function of temperature while the later measures transitions as a polymer responds to an applied oscillatory stress.

1.2 Effects on Glass Transition Temperature

The glass transition temperature marks the onset of backbone molecular motion as the polymer undergoes the transition from the solid glassy state to a rubbery material. There are numerous factors that affect the glass transition temperature such as chain flexibility, structure of the pendent groups, molecular weight, free volume and crosslinking.

Backbone structure is one of the most important factors that affects the T_g. The more flexible polymer chains possess a lower energy barrier to rotation and, thus, lower glass transition temperature. As an example, poly(dimethylsiloxane), PDMS, with a flexible silicone backbone has a very low T_g of -126 °C, while poly(benzimidazole), due to its rigid backbone and hindered rotations, has an extremely high T_g of 429 °C (Figure 2).

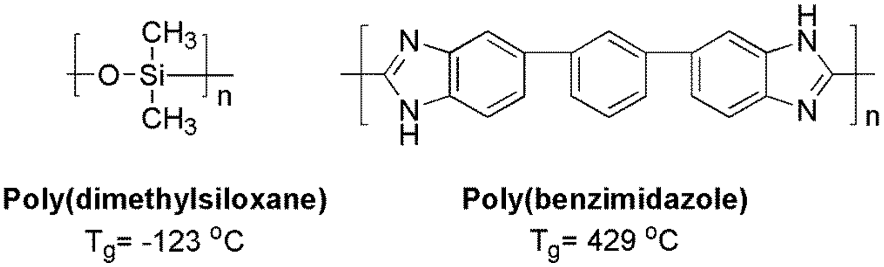


Figure 2. Effect of backbone structure on T_g.

Another important factor that affects the glass transition is the structure of any pendent groups attached to the polymer. Due to increased steric hindrance for rotation around sigma bonds, bulky side groups increase the T_g. For example, poly(1-butene), with a pendent ethyl group has low T_g of -24 °C while poly(styrene), with pendent phenyl groups, has a significantly higher T_g of 100°C. In general, flexible side groups lower T_g, as a result of more free volume, thus, allowing easier rotation in the backbone sigma bonds. In a series of poly(methacrylates) it is shown how the length of pendent alkyl chain decreases T_g from 105 °C in poly(methylmethacrylate) to as low as - 62 °C in poly(dodecyl methacrylates), (Figure 3).

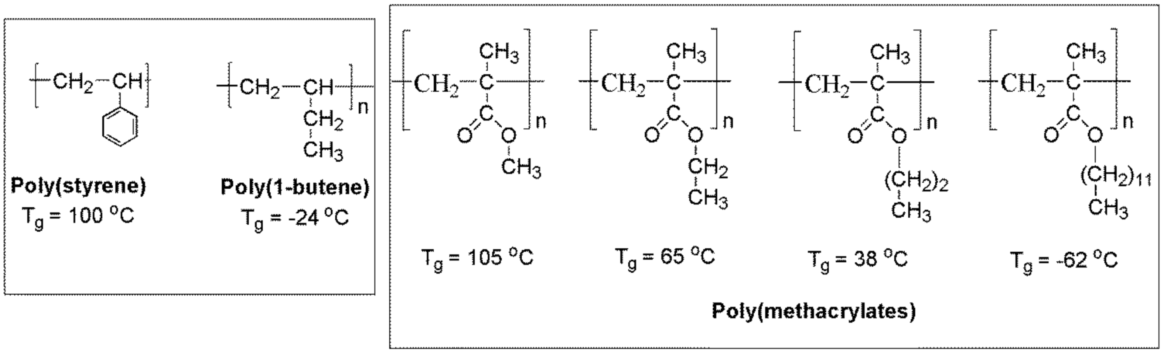


Figure 3. Effect of pendent group on T_g.

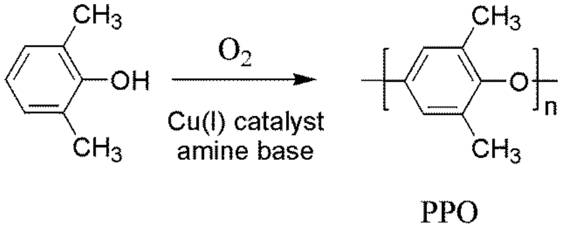
There are many other factors that affect the glass transition temperature such as molecular weight, free volume, crosslinking etc. In general, as the molecular weight of the polymer increases, the relative number of end groups decreases. Since the end groups are the least hindered units of polymer, as their percentage decreases there will be a concurrent increase in T_g. Crosslinking contributes to higher T_g as well by essentially tying the ends of the polymer chains down and restricting their mobility. Higher crosslinking density, number of crosslinks per main chain, makes the polymer more rigid, limiting the rotation and chain motions all of which increase T_g.

1.3 Poly(arylene ether)s

Poly(arylene ether)s, PAEs are high performance engineering thermoplastics utilized for a variety of applications. They have good mechanical properties, excellent resistance to hydrolysis and oxidation and high glass transition temperatures. PAEs are mostly prepared by nucleophilic aromatic substitution although they can be prepared by electrophilic aromatic substitution as well. A variety of functional groups can be introduced to these systems to meet the requirements for specific applications. The most common commercially available PAEs are: poly(phenylene oxide), PPO, poly(ether ether ketone), PEEK and poly(arylene ether sulfone), PAES.[2, 3]

1.3.1 Poly(phenylene oxide) PPO

Poly(2,6-dimethyl-1.4-phenylene oxide), PPO, is an engineering thermoplastic commercially introduced in 1964.[2] It is widely used because of its excellent mechanical properties maintained over a broad range of temperature (-45 to 120 °C). It has good resistance to oxidizing agents, a high glass transition temperature (T_g) of 208 °C, excellent hydrolytic stability and very low water absorption rate. PPO is synthesized by oxidative coupling polymerization of 2,6-dimethylphenol in the presence of cuprous chloride catalyst (Scheme 1).



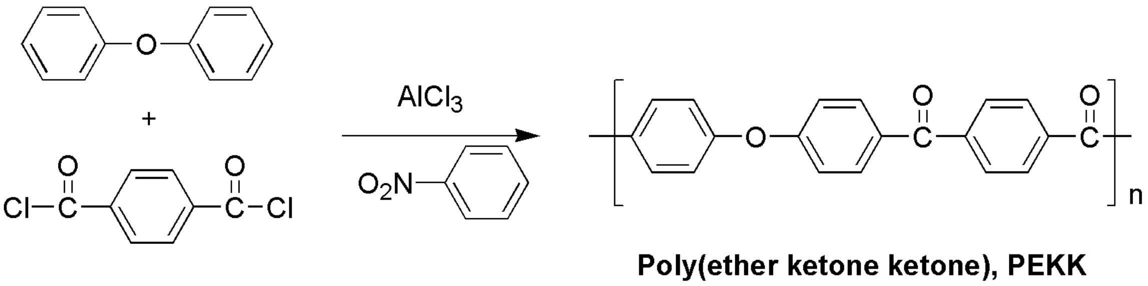
Scheme 1. Synthesis of PPO.

However, high processing costs have restricted PPO applications. To reduce costs of PPO it is mixed with the commodity plastic polystyrene to produce polymer blends known under the trade name Noryl®. There is a wide range of Noryl® polymer blends available providing a broad spectrum of materials with excellent properties.[2]

1.3.2 Poly(ether ether ketone), PEEK

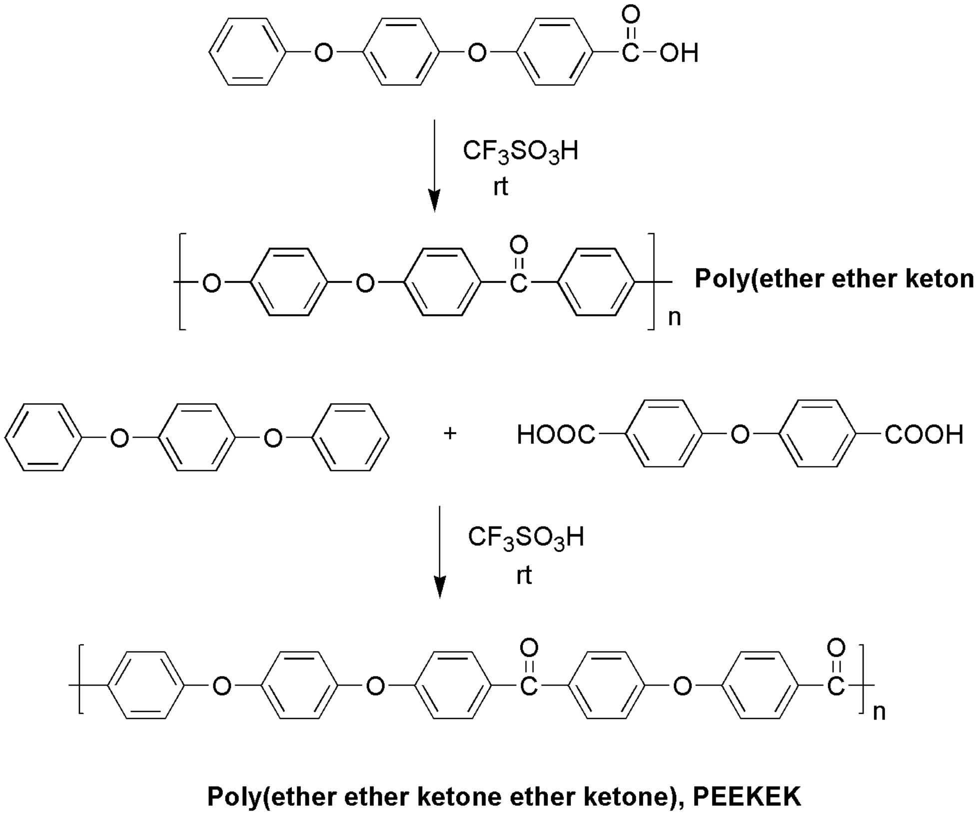
Poly (ether ether ketone), PEEK, is a semi-crystalline polymer with a T_g at 143 °C and T_m at 343 °C. Due to its completely aromatic structure it has high temperature performance and excellent mechanical properties and is used as engineering thermoplastic. PEEK has very low water absorption and is resistant to solvents although it can be dissolved in concentrated sulfuric acid.[2]

In 1962 Bonner reported the synthesis of completely aromatic poly(ether ketone), by Friedel Crafts polycondensation of diphenyl ether with terephthalyl chloride in nitrobenzene with aluminum chloride as catalyst (Scheme 2). However, because of insolubility in most of the organic solvents, the synthesized poly(ether ketone ketone), PEKK was low molecular weight polymer.[4]



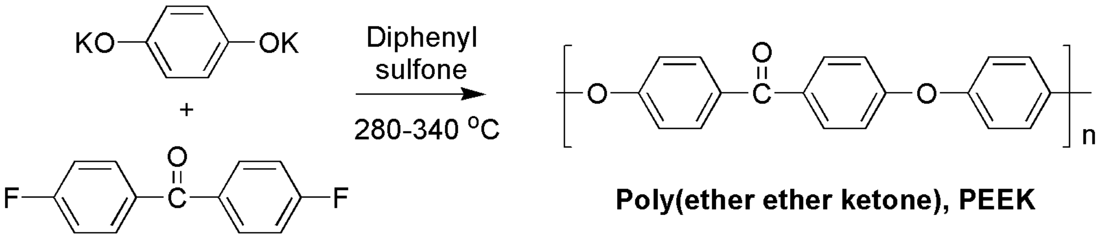
Scheme 2. Synthesis of PEKK by Friedel Crafts polycondensation.

Marks developed a system to synthesize PEK with higher molecular weight using liquid hydrogen fluoride as a solvent and BF_3HF complex as a catalyst.[5] In 1983 Rose prepared high weight PEK using trifluoromethanesulfonic acid to catalyze the condensation of carboxylic acid with phenyl ether (Scheme 3).[6] Due to the harsh reaction conditions and high cost these syntheses did not find wide application in industry.[7]



Scheme 3. Synthesis of PEEK and PEEKEK by EAS.

Atwood *et al* synthesized PEEK by nucleophilic aromatic substitution of dihalides using diphenylsulfone as solvent. To circumvent solubility issues and synthesize high molecular weight PEEK, the reaction temperature was kept close to the melting point of the polymer (280-340 °C).[8] Commercially PEEK is synthesized by nucleophilic aromatic substitution of 4,4'-diflourobenzophenone with the potassium salt of hydroquinone in diphenylsulfone (Scheme 4).[2]



Scheme 4. Synthesis of PEEK by NAS in diphenyl sulfone.

1.3.3 Poly(arylene ether sulfone)s, PAES

Poly(arylene ether sulfone)s, PAES are fully amorphous, aromatic engineering thermoplastic. They have high thermal stability (up to 400 °C), excellent resistance to hydrolysis and oxidation and high T_g due to their rigid backbone composed of aromatic ether linkages, aryl and sulfone groups. Because of their excellent properties they are used for a wide range of applications. The first commercially available PAES was synthesized in 1965 - by Union Carbide, known by its trade name UDEL®. Some of the commercially available PAES are illustrated in Figure 4. [9]

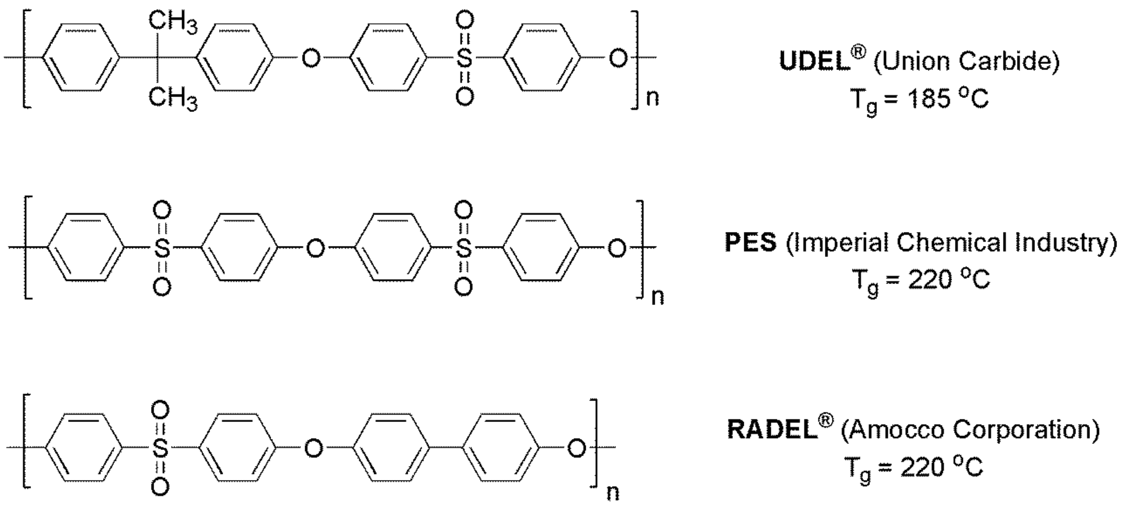
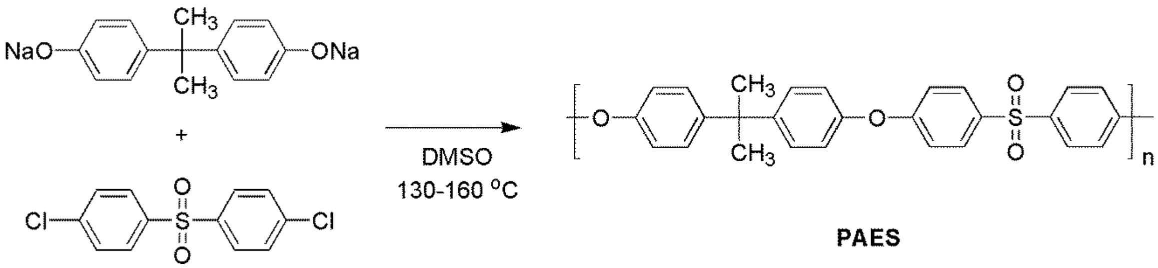


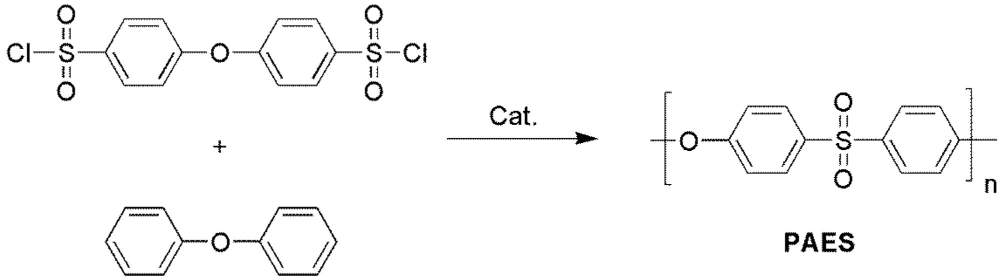
Figure 4. Some commercially available PAES.

PAES can be synthesized by electrophilic aromatic substitution, EAS[10] or nucleophilic aromatic substitution, NAS. The first NAS of PAES was done by Johnson *et al* in 1960s and it included two steps: conversion of bisphenol A into its salt and polycondensation with 4,4'-dichlorodiphenyl sulfone in the polar aprotic solvent dimethyl sulfoxide, DMSO (Scheme 5).[2, 9]



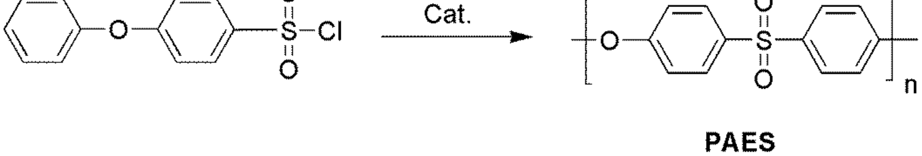
Scheme 5. Synthesis of PAES with Bisphenol A salt and 4,4'-dichlorodiphenylsulfone by NAS in DMSO.

Another route to synthesize PAES is via polysulfonation by an EAS process in which aryl sulfonyl chlorides react with aromatic nucleophiles to form sulphone linkages. It involves three steps: formation of sulfonylium ion by reaction of sulfonyl halide with a Lewis acid; electrophilic addition and proton abstraction. An example of EAS is the reaction of bis(4-chlorosulfonylphenyl)ether with diphenyl ether (Scheme 6).[9,10]



Scheme 6. Synthesis of PAES by EAS.

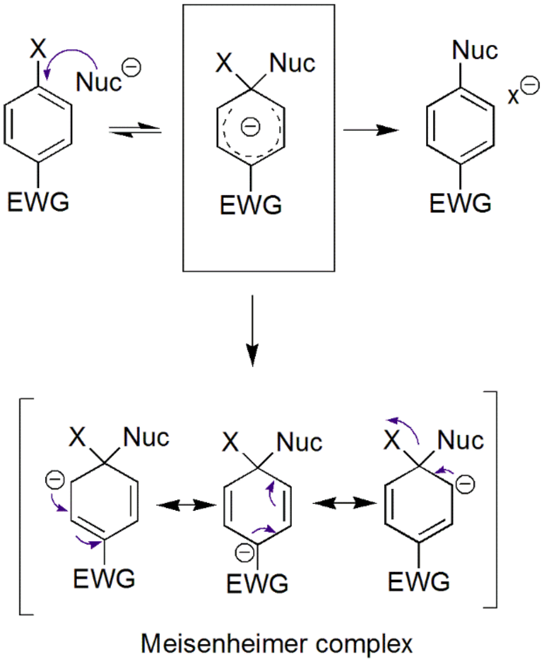
The backbone of PAES synthesized with this EAS was not always linear. To avoid branching in PAES an AB monomer, 4-chlorosulfonyldiphenylether, was used. (Scheme 7). This method provided PAES almost free from branching and. [9]



Scheme 7. EAS of a single AB monomer route for PAE.

1.4 Polycondensation by Nucleophilic Aromatic Substitution

Typically, PAEs are synthesized via nucleophilic aromatic substitution, NAS, a reaction that involves substitution of an aryl halide activated by a strong electron withdrawing group, EWG, located in the *ortho* or *para* position. The reaction occurs in two steps: nucleophilic attack at the *ipso* carbon and elimination of a good leaving group, halide. Nucleophilic attack is considered to be reversible and the rate-determining step, resulting in the formation of an anionic intermediate, known as Meisenheimer complex. The second step, considered irreversible, returns the aromaticity of the benzene ring with a concurrent loss of halide (Scheme 8). The EWG in NAS activates nucleophilic attack at the *ipso* carbon by decreasing the electron density and helps to stabilize the Meisenheimer complex. Many different EWG have been used including sulfone, ketone and phosphoryl groups.[11, 12]



Scheme 8. Mechanism for *para* activated NAS.

Although NAS is usually activated by EWG in the *para* position, *meta* positioned EWG has been reported to provide sufficient activation for NAS polycondesation. A variety of *meta* positioned EWG have been shown to sufficiently activate aryl fluorides for NAS. Our group has synthesized PAEs using *meta* activated 3,5-difluro monomers such as 3,5-difluorodiphenyl sulfone or 3,5-difluorobenzophenone. In these systems the activating group ends up pendent to the polymer backbone allowing the system introduction of functionality without directly altering the polymer backbone. Some of the *meta* activating EWG used in NAS reactions are shown are shown in Figure 5.[13, 14, 15]

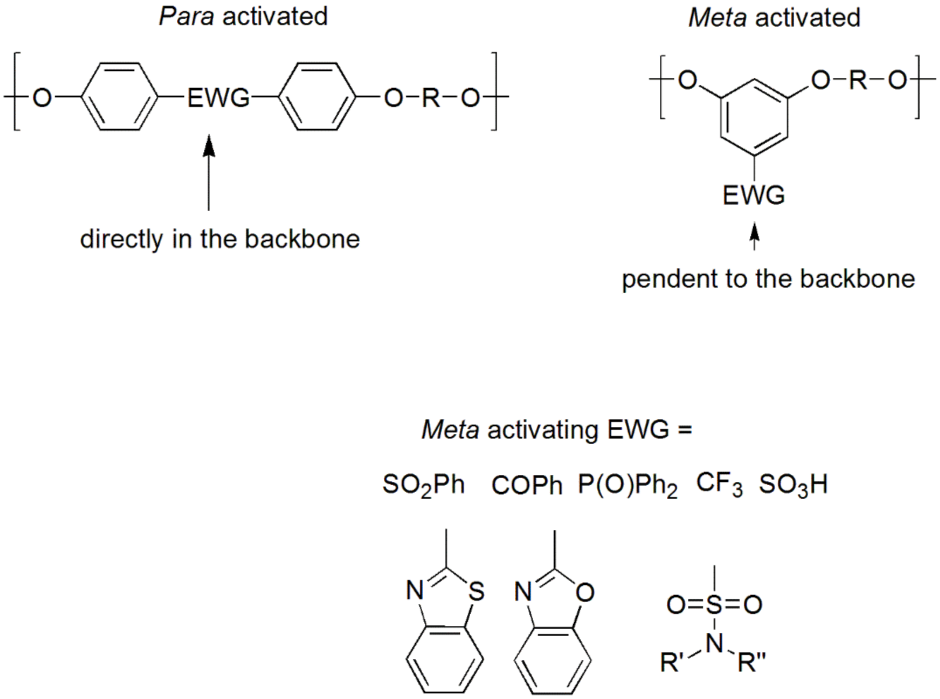


Figure 5. *Para* and *meta* activated systems.

1.5 “Pre” and “Post” modification chemistry

Introducing functionality into a polymer system can be a way to tailor physical and chemical properties to meet the requirements for specific applications. Functional groups can be introduced at the monomer stage (“pre”) or at the polymer stage (“post”) as shown in the Figure 6. ”Pre” modifications refers to modification prior to polymerization meaning that functional groups introduced must stay intact under the polymerization conditions and that side reactions must be avoided. To circumvent this, functional groups can also be introduced by “post” modification. However “post” modification has less control over the location and number of the functional groups.

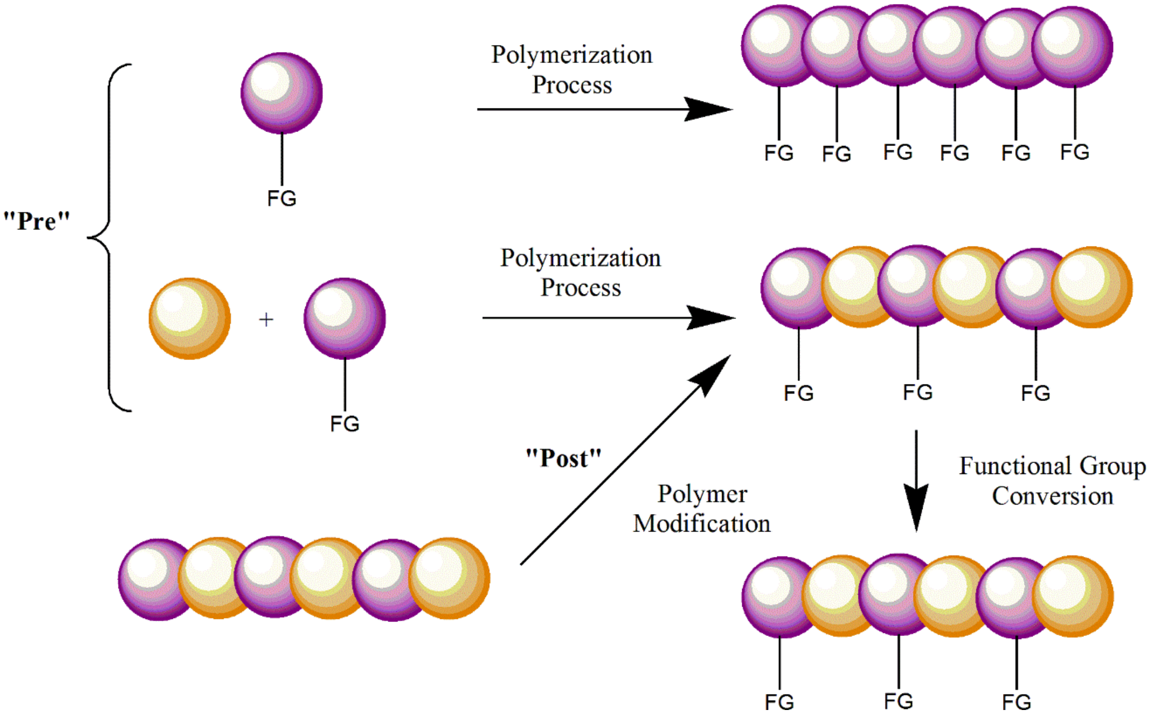


Figure 6. “Pre” and “post” modification.

1.6 Proton Exchange Membrane Fuel Cells (PEMFCs)

Because of the increasing use of non-renewable energy resources, fossil fuels, supplies are rapidly decreasing and so the need for alternative energy sources arises. An example of a renewable energy source is fuel cells, devices that convert chemical energy into electrical energy.[16] Different types of fuel cells are researched nowadays amongst which are polymer electrolyte membrane fuel cells (PEMFCs), direct methanol fuel cells (DMFCs), alkaline fuel cells (AFCs), molten carbonate fuel cells (MCFCs), solid oxide fuel cells (SOFCs) and regenerative fuel cells (RFCs) and phosphoric acid fuel cells (PAFCs).[17]

PEMFCs consist of an electrolyte, anode and cathode, both of which are usually platinum. The electrolyte is a solid polymer membrane that transfers protons from the anode to the cathode while electrons go through an external circuit as shown in Figure 7.

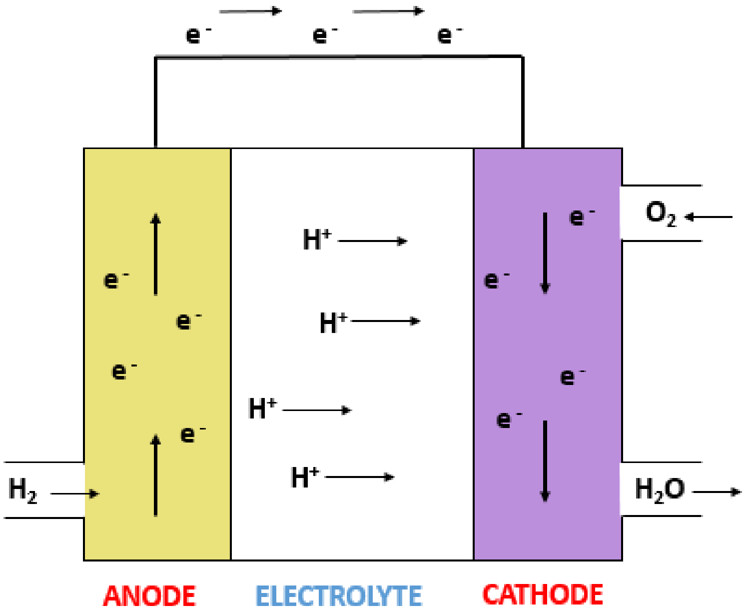


Figure 7. Schematic illustration of PEMFC.

At the anode hydrogen is oxidized and the liberated electrons flow through the external circuit and provide power while the protons are transferred to the cathode through the polymer electrolyte membrane. At the cathode protons are combined with the reduced oxygen and water is formed as the only byproduct. The polymer electrolyte membrane provides a barrier for fuel crossover. However, it is still permeable for CO produced as byproduct during production of hydrogen gas from reforming hydrocarbons and water that can potentially poison catalyst. CO catalyst poisoning is less common at high temperatures and almost completely reduced at 140 °C. [18] The reactions that occur on the electrodes are shown below:

Anode: $2\ H_2 \longrightarrow 4\ H^+ + 4\ e^-$

Cathode: $\underline{O_2 + 4\ H^+ + 4\ e^- \longrightarrow 2\ H_2O}$

Net reaction: $2\ H_2 + O2 \longrightarrow 2\ H_2O$ + energy

PEMFCs have been studied as an alternative energy source with many advantages such as portable application, high efficiency and power generation. In order to have high performance and become commercialized there are certain requirement that membranes need to fulfill such as high thermal stability, low water uptake, excellent resistance to hydrolysis and oxidation, good mechanical properties, low cost and low fuel crossover.

1.6.1 Ion Exchange Capacity and Water Uptake

The amount of water in PEMFCs is an important factor and it has a direct connection to the ion exchange capacity. Water in PEMFCs is used to facilitate proton transfer through hydrogen bonding. However too high a degree of hydration will result in membrane swelling and have a negative effect on the overall mechanical properties of PEMFCs. Insufficient hydration will cause drying of the membrane and lower proton conductivity. Thus it is very important to find a balance between sufficient ion exchange capacity and low water uptake.[19]

Water uptake is directly related to the concentration of ionic groups in the polymer that are responsible for conductivity such as sulfonic acid. Equivalent weight describes the relationship between moles of conducting ions and weight of dry polymer as shown in **Equation 1**:

$$EW\left(\frac{g}{equiv.}\right) = \frac{MW_{repeat\ unit}\ (\frac{g}{mol})}{moles_{acid}\ \ (\frac{mol}{equiv.})}$$

Equation 1. Equivalent weigh (EW) equation

EW is then used to determine ion exchange capacity (IEC) - the amount of acid in miliequivalents per gram of dried polymer as shown in **Equation 2**:

$$IEC\left(\frac{mequiv.}{g}\right) = \frac{1}{EW\ (\frac{g}{equiv.})}\ x\ 1000$$

Equation 2. Ion exchange capacity (IEC) equation.

IEC is a property that can be varied in order to find the balance between conductivity and water uptake. Higher IEC is related to higher proton conductivity, but also to higher water uptake, which results in swelling and in the end complete solubility of the membrane in water. Finding a perfect balance between IEC and WU results in a polymer with both high conductivity and the good mechanical properties required for use as a PEM. [20]

1.6.2 Nafion and its alternatives

Nafion® is a highly fluorinated polymer with a Teflon® backbone and sulfonic acid pendent groups (Figure 8). Due to its great properties, high proton conductivity with low water uptake, it is the most widely used material for PEM.

The high proton conductivity (90-120 mS/cm) of Nafion® membranes is due to the highly acidic perfluorosulfonic groups with low a pK_a of -3.09. Nafion is also highly resistant to oxidation and hydrolysis.

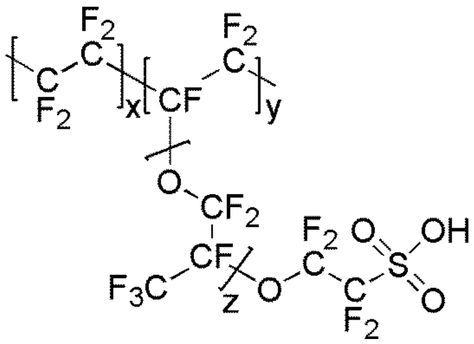


Figure 8. Nafion® – general chemical structure.

Nafion® is recognized to have a good balance between moderately low water uptake and high proton conductivity due to its ability to microphase separate. Its highly hydrophobic backbone and pendent hydrophilic acid groups form structures similar to reverse micelles, called water channels through which protons are conducted. Maintaining a low amount of acid groups incorporated in the polymer limits its water uptake.[20]

However, there are some drawbacks with Nafion® for PEMs: high cost (~$800/m^2), low conductivity and high fuel crossover at temperatures above 80°C and low glass transition temperature. This prohibits its use in high temperature PEMFC, above 100 °C.[18, 19]

Although Nafion® has been used in the space program [21] and many other applications, due to its disadvantages, there is a need for other potential high performance and low cost candidates for PEMs. Many different alternatives have been studied such as poly(ether ether ketone)s (PEEK), poly(aryl ether sulfone)s (PAES), poly(phenylene oxide)s (PPO), poly(arylene ether sulfone amide)s (PAESA). [19, 20]

Because of their properties such as high thermal stability, resistance to both hydrolysis and oxidation, and low cost, PAEs have been widely investigated for use as PEMs. They can be easily functionalized either directly in the backbone or pendent with proton conducting groups such as sulfonic acid, phopshonic acid or carboxylic acid. These acids have low affinity for protons so they are good proton conductors. Sulfonic acid is the strongest acid with lowest proton affinity and thus the best proton conductor.

The sulfonyl group can be introduced in polymers by “pre” or “post” modification. In 1976, Noshay and Robeson used “post” modification to sulfonate commercially available polysulfone.[22] However “post” sulfonation provides less control over degree of sulfonation and there is a possibility of side reactions and polymer degradation under the harsh conditions necessary for functionalization. By sulfonating at the monomer stage, those disadvantages can be avoided, although it requires some additional steps.[19] It has also been shown that pre-sulfonated systems have higher conductivity than post sulfonated, due to thetter separation between sulfonyl groups.[23, 24]

The sulfonic acid group can be introduced directly to the backbone or pendent. Our group has reported the synthesis of poly(arylene ether) with pendent sulfonyl group and compared the properties with a PAE sulfonated directly on the backbone at similar IEC values the PAEs with pendent substitution had lower WU and higher conductivity.[25] Addition of the sulfonyl group pendent to the backbone also might improve hydrolytic and oxidative stability.

1.7 Current work

This current work is divided into two separate projects both of which are based on functionalization of PAEs with a sulfonyl group pendent to the backbone. The first project involves sulfone based PAEs with sulfonic group introduced, as potential candidates for PEMs. The second project involves PAEs as well, but with the sulfonamide group as a strong activating group for NAS and using the ”pre” functionalization method to tailor their thermal properties.

1.7.1 Sulfone Based PAEs

Sulfone based PAEs have been investigated as a potential alternatives to Nafion® for use as PEMs. Despite its exceptional properties Nafion® has few drawbacks, such as high cost, fuel crossover and low conductivity at high temperatures above 80 °C. This project is designed to use different strategies to synthesize PAEs that will be used as PEM without some of the limitations that Nafion® possesses.

One of the most important features for PEMs, besides high proton conductivity, is the balance between high IEC and low water uptake. Different conducting groups that can be incorporated in PAEs, to the backbone or pendent, such as: sulfonic, phosphoric and carboxyl groups. Studies have shown that groups that are pendent to the backbone are more easily accessed, hydrolytically more stable and, as our group has shown in some previous studies, improve proton conductivity (Figure 9). [21]

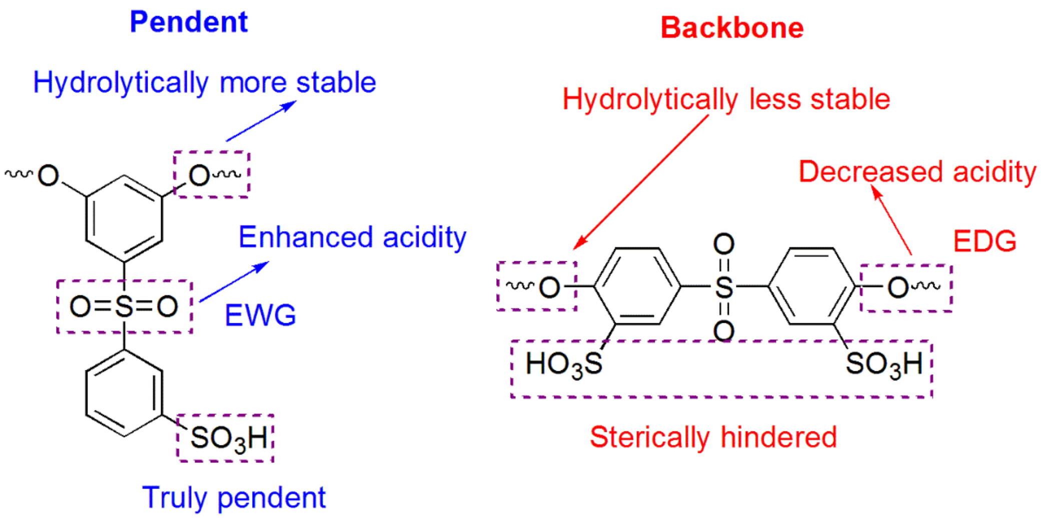


Figure 9. Pendent vs. backbone functionalization.

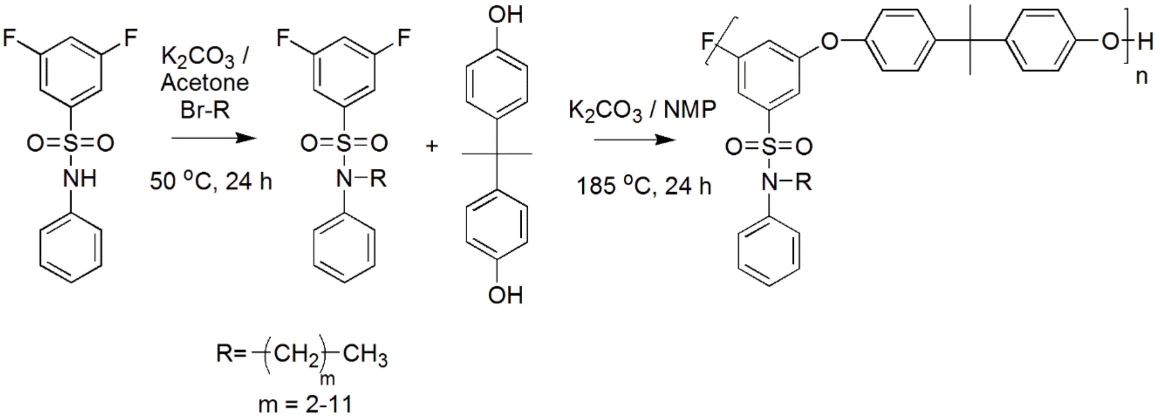
The goal was to prepare a series of PAE with pendent acid groups attached that will meet the needs for use as PEM. A series of PAES carrying pendent sulfonic groups, with varying IECs were prepared. The IEC varied from 0.91 for copolymers to 1.58 for a homopolymer with 3-sulfonated-3,5 diflourodiphenylsulfone and Bisphenol AF. With the previous study that our group has made it has been shown that Bisphenol AF based PAES with an IEC of 1.56 had a significantly higher proton conductivity of 266 mS/cm than Nafion® with proton conductivity of 120 mS/cm.

The newly synthesized PAES have been purified and preliminary characterization data has been acquired.

1.7.2 Sulfonamide Based PAEs

Sulfonamides have been widely studied for pharmaceutical uses. Their very strong EWG character has only recently been used in nucleophilic aromatic substitution polycondensations by activating the aryl halides in the *ortho* and *para* positions[26] as well as in the *meta* position[27]. The sulfonamide moiety provides a site for the introduction of a wide range of chemical diversity that can be utilized to tailor physical properties.

This project is based on the alkylation of *N*-phenyl-3,5-difluorobenzene sulfonamide, as a starting material, with chain lengths of 3 to 12 carbon atoms followed by conversion to the desired PAEs (Scheme 9). The goal was to utilize alkyl chain length to tune the glass transition temperatures while maintaining good thermal stability of newly synthesized PAEs.



Scheme 9. Synthetic route for series of sulfonamide based PAEs.

2. EXPERIMENTAL

2.1 Instrumentation

^1H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were acquired using a Bruker AVANCE 300 MHz instrument operating at 300 and 75.5 MHz, respectively. Samples were dissolved in an appropriate deuterated solvent (DMSO-d_6 or $CDCl_3$) at a concentration of (~ 30 mg / 0.7 mL). GC/MS analyses were performed using a Hewlett-Packard (HP) 6890 Series GC and a HP 5973 Mass Selective Detector/Quadrupole system. DSC and TGA analysis were carried out on TA Instruments DSC Q200 (under nitrogen) and TGA Q500 (under nitrogen or air), respectively, at a heating rate of 10 ºC/ min. Size Exclusion Chromatography (SEC) analysis was performed using a system consisting of a Viscotek Model 270 Dual Detector (viscometer and light scattering) and a Viscotek Model VE3580 refractive index detector. Two Polymer Laboratories 5 μm PL gel Mixed C columns (heated to 35 ºC) were used with tetrahydrofuran/5% (v/v) acetic acid as the eluent and a GPC max VE-2001 with pump operating at 1.0 mL/minute. Number average molecular weights, M_n, and the dispersity were determined with the RI signal (calibrated with polystyrene standards). Melting points were determined on a MEL-TEMP apparatus and are uncorrected. Elemental analyses were obtained from Midwest Microlabs, Inc., Indianapolis, IN.

2.2 Materials

N-Methylpyrrolidinone (NMP) was purchased from Sigma Aldrich Chemical Co. and was dried over CaH_2 and distilled under nitrogen prior to use. Reagent-grade anhydrous potassium carbonate powder (K_2CO_3) was purchased from Sigma Aldrich Chemical Co. and dried at 130 °C in an oven prior to use. 3,5-Difluorodiphenyl sulfone , was synthesized via the previously reported route.[28] Bisphenol A and Bisphenol AF were purchased from Sigma Aldrich Chemical Co., recrystallized from toluene, and dried *in vacuo* prior to use. 4,4-Diflourodiphenylsulfone was purchased from Sigma Aldrich Chemical Co., recrystallized from toluene, and dried *in vacuo* prior to use. Tetrahydrofuran (THF), dichloromethane (DCM), and isopropyl alcohol (IPA) were used as received from Avantor. Chloroform ($CHCl_3$), fuming sulfuric acid (H_2SO_4) and toluene were purchased from VWR and used as received. ACS-certified acetone, sodium bicarbonate ($NaHCO_3$) and magnesium sulfate ($MgSO_4$) were used as received from Fischer Scientific. Bromoalkanes, aniline, deuterated dimethylsulfoxide (DMSO-d_6) and deuterated chloroform ($CDCl_3$) were purchased from Sigma Aldrich and used as received. Non-iodized Morton salt was purchased from a local retailer and used as received.

2.3 Synthesis of 3-sulfonated-3,5’-difluorodiphenyl sulfone, 1c

To a 25 mL round bottom flask, equipped with a magnetic stir bar and condenser, were added 7.01 g (27.55 mmol) of 3, 5-difluorodiphenylsulfone and 12.4 mL of fuming sulfuric acid. The reaction mixture was placed in an oil bath and heated to 70°C for 6 h at which point an aliquot was taken and precipitated in water. The material was completely soluble indicating that the sulfonation reaction had reached completion. The entire reaction mixture was then added to 500 mL of vigorously stirred water, followed by “salting out” the desired compound using NaCl. The resulting organic material was isolated via filtration. The solids were re-dissolved in water and adjusted with 5M NaOH to pH 6.5 and “salted out” again using NaCl. The resulting solids were isolated by vacuum filtration and recrystallized from 9:1 solution of isopropanol/water to afford 5.6 g (57%) of **1c.**

Proton NMR specatral data was in agreement with the literature.[25]

2.4 Representative Homopolymer synthesis procedure, 2a

Via step growth polymerization a homopolymer derived from 3-sulfonated -3’, 5’-difluorodiphenylsulfone and Bisphenol AF was synthesized. To a 5 mL round bottomed flask (RBF), equipped with condenser, stir bar, nitrogen inlet and Dean-Stark trap, were added 3-sulfonated-3’,5’-difluorodiphenylsulfone (0.52 g, 1.4 mmol), Bisphenol AF (0.47 g, 1.4 mmol), K_2CO_3 (0.58 g,4.2 mmol), 2.2 mL of toluene (azeotropic drying agent) and 2.2 mL of NMP. The reaction was heated to 150°C for 4 h to dehydrate the system. After azeotropic drying, the toluene was removed and the mixture was heated to 180°C for 16 h for polymerization via nucleophic aromatic substitution to take place. The reaction mixture was cooled to room temperature, diluted with 2 mL of NMP and then added dropwise to a 400 mL of vigorously stirred distilled water. The resulting white string-like precipitate was isolated via filtration, followed by drying under vacuum in a drying pistol to afford 0.697 g (78.8%) of polymer **2a** as a white solid. DEPT 90 ^{13}C NMR (DMSO-d_6, δ): 112.8, 114.2, 118.8, 124.2, 127.8, 129.8, 131.1,131.7.

2.5 Representative Random Copolymer Synthesis Procedure, 2b-e

Random copolymers with different IEC values were synthesized by polymerization of varying ratios of 3-sulfonated-3,5’-diflorodiphenylsulfone and 4.4-diflorodiphenylsulfone with Bisphenol AF. A copolymer with IEC = 0.91, **2e**, was synthesized as follows: to a RBF, equipped with condenser, stir bar, nitrogen inlet and Dean-Stark trap, were added: 4, 4-difluorodiphenylsulfone (0.16 g, 0.72 mmol), Bisphenol AF (0.47 g, 1.4 mmol), 3’-sulfonated-3,5-difluorodiphenylsulfone (0.26 g, 0.68 mmol), K_2CO_3 (0.58 g , 4.2 mmol), 2.2 mL of toluene (azeotropic drying agent) and 2.2 mL of NMP. The reaction was heated to 150°C for 4 h to dehydrate the system. After azeotropic drying, the toluene was removed and the mixture was heated to 180 °C for 16 h for polymerization via nucleophilic aromatic substitution to take place. The reaction mixture was cooled to room temperature, diluted with 2 mL NMP and then added dropwise to a 400 mL of vigorously stirred distilled water. The resulting white string-like precipitate was isolated via filtration, followed by drying in drying pistol to afford 0.559 g (67.6%) of polymer as a white solid. The polymer was reprecipitated by dissolving in DMSO and slowly adding the solution to isopropanol. The isolated polymer was dried again in a drying pistol.

All polymers with varying IEC values (IEC = 1.10, 1.28 and 1.46) were synthesized following the same procedure with the same reaction conditions. The following yields were obtained: **2b** 64%, **2c** 55.5%, **2d** 59 %.

NMR peaks for all polymers had the same chemical shifts as the one reported above with varying intensities depending on the ratio of the monomers used.

2.6 Synthesis of *N*-phenyl-3,5-difluoro benzene sulfonamide, 3a

In a 250 mL Erlenmeyer flask, equipped with a stir bar, were placed 3,5 difluorobenzene sulfonyl chloride (10 g, 47.2 mmol), $NaHCO_3$ (6.7 g, 80.1 mmol) and 25 mL of DCM. To the vigorously stirred reaction mixture was added aniline (4.30 mL, 47.2 mmol) in dropwise fashion. The reaction mixture was allowed to react for 45 minutes at room temperature at which point 50 mL of DCM was added and the organic layer was washed with H_2O (3x50 mL), 1 M HCl (25 mL), 0.05 M NaOH (50 mL) and H_2O (2x 50 mL).The organic layer was dried over $MgSO_4$, filtered and the solvent was removed via rotary evaporation to afford the crude product which was recrystallized from EtOH/H_2O, to afford 8.40 g (66 %) of white crystals. ^1H($CDCl_3$, δ): 6.71 (s, 1H), 6.91 (tt, 1H), 7.03 (m,2H), 7.11 (tt, 1H), 7.22 (m, 4H).^{13}C NMR ($CDCl_3$, δ): 108.6, 110.6, 122.2, 126.2, 129.5, 135.4, 142.1, 162.6 ppm.

2.7 Synthesis of *N*-alkyl-*N*-phenyl sulfonamides, 4a-f

A representative procedure for *N*-propyl-*N*-phenyl sulfonamide, **4a**, is as follows: to a 10 mL RB flask, equipped with condenser, stir bar and nitrogen inlet were added: *N*-phenyl-3,5-difluorobenzene sulfonamide (1.01 g, 3.72 mmol), 5 mL of acetone, K_2CO_3 (0.87 g, 6.32 mmol) and 1-Bromopropane (0.34 mL, 3.72 mmol). The reaction mixture was heated to 50°C for 24 hours at which point it was cooled to room temperature, diluted with chloroform (15 mL) and extracted with water (3 x 30 mL). The aqueous layers were extracted with 3 x 30 mL of chloroform. The organic layers were combined and dried over $MgSO_4$ and filtered. The solvent was removed via rotary evaporation to afford the crude product. The resulting solid was recrystallized from EtOH/H_2O to afford 0.859 g (74 %) of a white solid. ^1H NMR ($CDCl_3$, δ): 0.96 (t, 3H), 1.47 (m, 2H), 3.56 (t, 2H), 7.03 (tt, 1H), 7.05 (m, 2H), 7.15 (m, 2H), 7.35 (m, 3H), ^{13}C NMR ($CDCl_3$, δ): 10.9(s), 21.5(s), 52.7(s), 108.0 (t), 111.0 (dd), 128.6 (s), 129.2 (s), 129.5 (s), 138.3 (s), 141.8 (t), 162.5 (dd). Elemental Analysis: Calc. Anal. for $C_{15}H_{15}F_2NSO_2$: C, 57.8; H, 4.86; Found: C, 57.84; H, 4.80.

The remaining *N*-alkyl-*N*-phenyl sulfonamides were synthesized following the same procedure followed by recrystallization from EtOH/H_2O and drying in vacuo.

4b (70 %): ^{1}H NMR ($CDCl_3$, δ): 0.89 (t, 3H), 1.40 (m, 4H), 3.58 (t, 2H), 7.03 (tt, 1H), 7.07 (m, 2H), 7.14 (m, 2H), 7.35 (m, 3H). ^{13}C NMR ($CDCl_3$, δ): 13.5(s). 19.5(s), 30.3(s), 50.7(s), 108.0 (t), 111.0 (dd), 128.3 (s), 128.6 (s), 129.2 (s), 138.3 (s), 141.7 (t),162.5 (dd). Elemental Analysis: Calc. Anal. for $C_{16}H_{17}F_2NSO_2$: C, 59.06; H, 5.27; Found: C, 59.35; H, 5.35.

4c (70 %):^{1}H NMR ($CDCl_3$, δ): 0.87 (t, 3H), 1.23 (m, 8H), 1.44 (p, 2H), 3.57 (t, 2H), 7.03 (tt, 1H), 7.07 (m, 2H), 7.14 (m, 2H), 7.35 (m, 3H). ^{13}C NMR ($CDCl_3$, δ): 14.0 (s), 22.5 (s), 26.2 (s), 28.2 (s), 28.7 (s), 31.6 (s), 51.0 (s), 108.0 (t), 111.0 (dd), 128.3 (s), 128.6 (s), 129.2 (s), 138.3 (s), 141.7 (t), 162.5 (dd). Elemental Analysis: Calc. Anal. for $C_{19}H_{23}F_2NSO_2$: C, 62.10; H, 6.31; Found: C, 61.99; H, 6.25.

4d (69%): ^{1}H NMR ($CDCl_3$, δ): 0.88 (t, 3H),1.23 (m, 10H),1.44 (p, 2H), 3.58 (t, 2H), 7.03 (tt, 1H), 7.07(m, 2H), 7.15 (m, 2H), 7.35 (m, 3H). ^{13}C NMR ($CDCl_3$, δ): 14.0(s), 22.6 (s), 26.3 (s), 28.2 (s), 29.0 (s), 29.1 (s), 31.7 (s), 51.0 (s), 108.0 (t), 111.0 (dd), 128.3 (s), 128.6 (s), 129.2 (s), 138.3 (s), 141.8 (t), 162.5 (dd). Elemental Analysis: Calc. Anal. for $C_{20}H_{25}F_2NSO_2$: C, 62.97; H, 6.61; Found: C, 63.09; H, 6.64.

4e (72 %):^{1}H NMR ($CDCl_3$, δ): 0.89 (t, 3H), 1.24 (m, 16H), 1.44 (p, 2H), 3.57 (t,3H), 7.03 (tt, 1H), 7.07(m, 2H), 7.13(m,2H), 7.35 (m, 3H). ^{13}C NMR ($CDCl_3$, δ): 14.0(s), 22.6 (s), 26.3 (s), 28.2 (s), 29.0 (s), 29.3 (s), 29.4 (s), 29.5 (s), 29.6 (s), 31.9 (s), 51.0 (s), 108.0 (t), 111.0 (dd), 128.3 (s), 128.6 (s), 129.2 (s), 138.3 (s), 141.8 (t), 162.5 (dd). Elemental Analysis: Calc. Anal. for $C_{23}H_{31}F_2NSO_2$: C, 65.22; H, 7.38; Found: C, 65.30; H, 7.48.

4f (73%):^{1}H NMR ($CDCl_3$, δ): 0.89 (t, 3H), 1.24 (m, 18 H),1.44 (p, 2H), 3.58 (t, 2H), 7.03 (tt, 1H), 7.06 (m,2H), 7.15 (m, 2H), 7.35 (m, 3H). ^{13}C NMR ($CDCl_3$, δ): 14.0(s), 22.6(s), 26.3(s), 28.2(s), 29.0(s), 29.3(s), 29.4(s), 29.5(s), 29.5(s), 29.6(s), 31.9(s), 51.0(s), 108.0 (t), 111.0 (dd), 128.3 (s), 128.6 (s), 129.2 (s), 138.3 (s), 141.7 (t), 162.5 (dd). Elemental Analysis: Calc. Anal. for $C_{24}H_{33}F_2NSO_2$: C, 65.87; H, 7.60; Found: C, 65.89; H, 7.67.

2.8 Polymerization of 4a-f using Bisphenol A to form 5a-f

A series of polymers derived from *N*-alkyl-*N*-phenyl-3,5-difluorobenzene sulfonamide with different alkyl chain lengths and Bisphenol A were synthesized under typical NAS conditions. As a representative example, the synthesize of the *N*-propyl-*N*-phenyl-sulfonamide, **5a**, PAEs was as follows: to a 5 mL round bottomed flask (RBF), equipped with condenser, stir bar, nitrogen inlet, were added *N*-propyl-*N*-phenyl sulfonamide (311 mg, 1 mmol), Bisphenol A (228 g, 1mmol), K_2CO_3 (414 mg, 3 mmol) and 1.56 mL of NMP. The reaction was heated to 185°C for 24 h, at which point the reaction mixture was cooled to room temperature, diluted with 2 mL of THF and then added dropwise to 400 mL of vigorously stirred distilled water. The resulting precipitate was isolated via filtration, followed by air- drying on the filter paper and afterwards in a drying pistol. The solids were dissolved in chloroform and precipitated from isopropanol to afford 0.355 g (74 %) of a white solids. ^{13}C NMR ($CDCl_3$, δ): 10.9, 21.5, 30.9, 42.3, 52.4, 111.0, 112.2, 119.4, 127.8, 128.3, 128.6, 129.0, 138.7, 140.6, 146.6, 153.4, 159.1.

5b (70%): ^{13}C NMR ($CDCl_3$, δ): 13.5, 19.5, 30.9, 42.3, 50.4, 111.0, 112.2, 119.0, 127.8, 128.3, 128.6, 129.0, 138.7, 140.5, 146.7, 151.5, 153.4, 159.1.

5c (69%): ^{13}C NMR ($CDCl_3$, δ): 14.0, 22.5, 26.3, 28.2, 28.7, 31.0, 31.6, 42.32, 50.71, 111.0, 112.2, 119.0, 127.8, 128.3, 128.6, 128.9, 138.8, 140.6, 146.6, 153.4, 159.1.

5d (70%):^{13}C NMR ($CDCl_3$, δ): 14.4, 22.5, 26.3, 28.2, 29.0, 29.1, 30.9, 31.7, 42.3, 50.7, 111.0, 112.2, 119.0, 127.7, 128.3, 128.5, 128.9, 138.7, 140.5, 146.6, 153.4, 159.1.

5e (80%):^{13}C NMR ($CDCl_3$, δ): 14.1, 22.6, 26.3,28.2, 29.0, 29.2, 29.4, 29.5, 29.6,31.0,31.8, 42.3,50.7,111.0, 112.2, 119.0, 127.8, 128.3,128.6, 128.9, 138.8, 140.6, 146.6, 153.4, 159.1.

5f (72%):^{13}C NMR ($CDCl_3$, δ): 14.1, 22.6, 25.3, 26.3, 28.2, 29.1, 29.3, 29.4, 29.5, 29.6, 31.0, 31.9, 42.3, 50.7, 64.42, 111.0, 112.2, 119.0, 127.8, 128.9, 138.8, 140.5, 146.6, 153.4, 159.1.

2.9 Characterization

2.9.1 Thermogravimetric Analysis (TGA)

The thermo oxidative stability of the polymers was investigated using a TA Instruments Q500 Thermogravimetric Analyzer. The method that was used included heating a 5 mg of sample at a rate of 10°C/min from 40°C to 750°C under nitrogen or air atmosphere. The weight loss was recorded as a function of time and the thermal stability was reported as % weight loss.

2.9.2 Differential Scanning Calorimetry (DSC)

A TA Instruments Q200 Differential Scanning Calorimeter was used to determine any thermal transition temperatures. A typical method included heating 5 mg of sample, in Tzero aluminum pan, at 10 ºC/min from 40 ºC to 300 ºC and cooling at 20 ºC/min to 40 ºC in two cycles under a nitrogen atmosphere. The glass transition temperature, T_g, was determined at the midpoint of the tangent of the second heating cycle. The first heating cycle was utilized to erase the thermal history of the polymers.

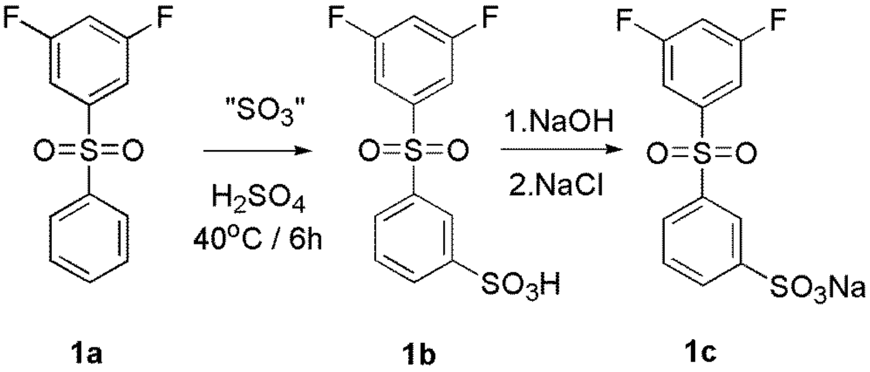
2.9.3 Size Exclusion Chromatography (SEC)

Size exclusion chromatography was used to determine molecular weight and molecular weight distributions of polymers for polymers soluble in THF/5% acetic acid. Number average molecular weights and the polydispersity index (PDI) were determined using the refractive index (RI) signal, the weight average molecular weight were determined via light scattering signal. Calibration was done using polystyrene standards.

3. RESULTS AND DISCUSSION

3.1. Synthesis of 3-sulfonated-3’5’-difluorophenylsulfone, 1c

The synthesis of 3-sulfonated-3’5’-difluorodiphenyl was carried out via EAS by a two-step process as shown in Scheme 10.



Scheme 10. Synthesis of 3-sulfonated-3’5’-diflurodiphenylsulfone, **1c.**

3,5-Diflurordiphenyl sulfone, **1a** was treated with fuming sulfuric acid at 40 °C for 6 h, which led to sulfonation of the monomer *meta* to the sulfone group, **1b**. The second step included neutralization with NaOH and “salting out” providing the salt form, **1c,** of the desired monomer. A final recrystallization from a mixture of isopropanol and water (9:1) provided 5.6 g (57 %) of **1c** as a white, fibrous solid.

To confirm the monomer structure ^{1}H and ^{13}C NMR spectra were obtained and they were in good agreement with literature values. [25]

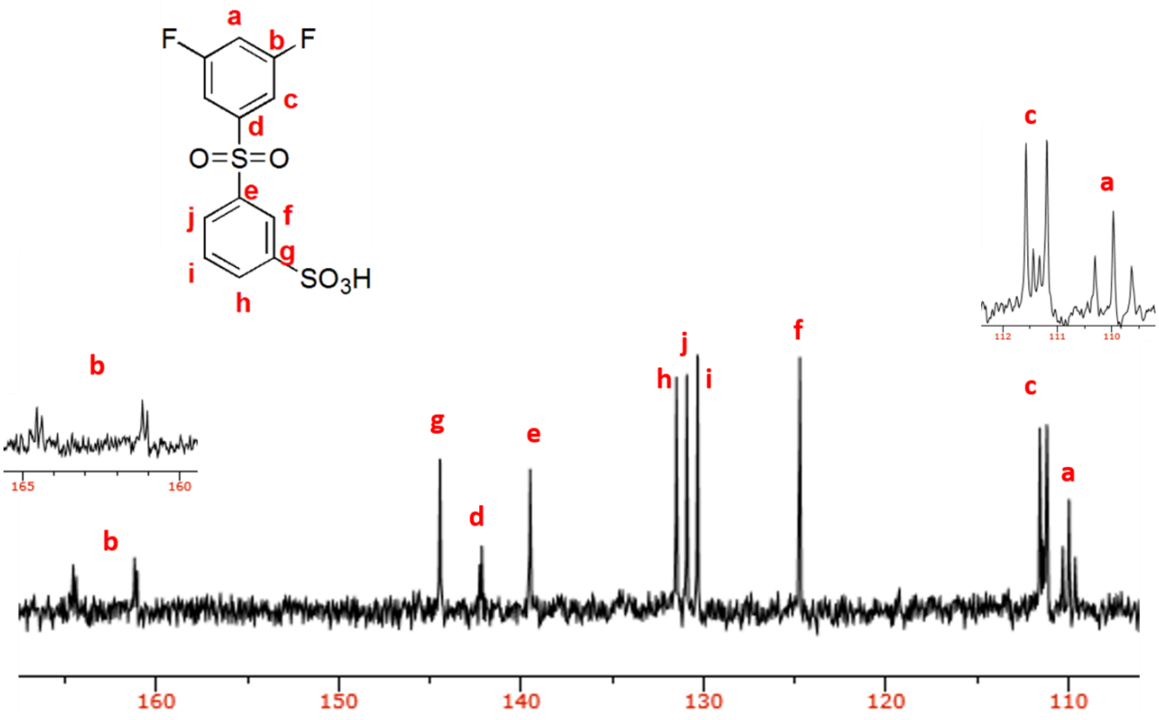
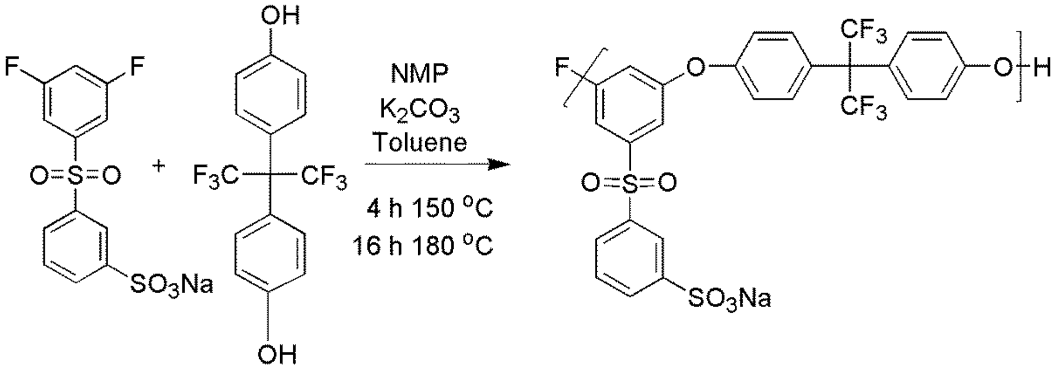


Figure 10. 75.5 MHz ^{13}C NMR ($CDCl_3$) spectrum of monomer **1c**.

The^{13}C NMR spectrum of monomer **1c** is shown in Figure 10. Peaks **a**, **b**, **c** and **d** arise from the carbon atoms on the upper, fluroinated phenyl ring and all appear as multiplets due to the coupling with two *meta* fluorines. Peak **a** is a triplet at 109.9 ppm, coupled with two fluorine with equal J values ($^{2}J_{C\text{-}F}$ = 25.4 Hz). Peaks **b** at 164.4 ppm ($^{1}J_{C\text{-}F}$ = 253.4 Hz, $^{3}J_{C\text{-}F}$ = 11.72 Hz) and **c** at 111.3 ppm ($^{2}J_{C\text{-}F}$ = 18.6 Hz, $^{4}J_{C\text{-}F}$ = 10.1 Hz) are doublets of doublets due to the coupling with two non-equivalent fluorines. Carbon **d** appears as a triplet at 142.2 ppm ($^{3}J_{C\text{-}F}$ = 8.48 Hz), carbons **g, e, f, h, j** and **i** are all singlets at 144.4, 139.5, 131.4, 130.9 130.3 and 124.7 ppm, respectively.

3.2 Homopolymer synthesis, 2a

The first polymer, out of the series of sulfonated PAES, was homopolymer with an IEC of 1.58 meq/g. It was prepared via NAS polycondensation with Bisphenol AF as the nucleophilic reaction partner and difluoro monomer **1c** as the electrophile as shown in Scheme 11. Usually PAES are synthesized with the EWG located *para* to the leaving group, but use of a very strong EWG, such as sulfone allows NAS to occur in the *meta* position as well. The initial ratio of monomer and Bisphenol AF was slightly unbalanced due to the hygroscopic nature of monomer **1c**. The amount of moisture present in the monomer was determined using TGA and the weight of monomer used for polymerization was corrected as necessary. The homopolymer was precipitated from water, dissolved in NMP, reprecipitated from isopropanol and dried under vacuum.



1c **2a**

Scheme 11. Homopolymer synthesis **2a**.

The polymer structure was confirmed with ^{1}H and ^{13}C DEPT90 NMR spectroscopy. The ^{13}C DEPT90 NMR spectrum of homopolymer **2a** is shown in Figure 11. There are 8 different signals present representing 8 different CH groups. Signals **a** at 114.2 ppm and **b** at 112.8 ppm, appear as singlets which proves that the fluorines have been displaced in the polymerization process and there is no more coupling with the carbons. Two additional peaks appear in the spectrum, **g** at 118.8 ppm and **h** at 129.8 ppm that correspond to CH groups on phenyl moiety of Bisphenol AF. The carbons on the bottom the phenyl ring c, d, e and f are all singlets at 124.2, 131.7.127.8, 129.8 ppm, respectively.

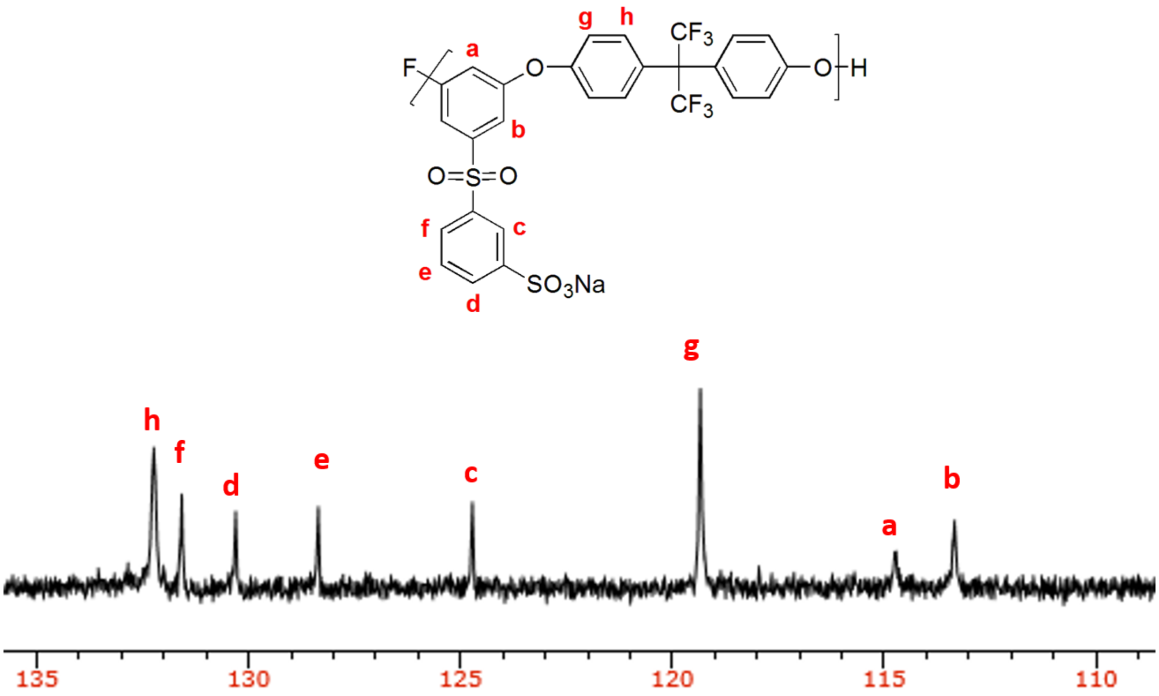


Figure 11. 75.5 MHz DEPT 90 ^{13}C NMR spectrum (DMSO-$_{d6}$) of **2a**.

3.3. Random copolymer synthesis, 2b-e

A series of Bisphenol AF-based copolymers with varying IEC values was synthesized. The desired IEC values were achieved by varying the ratios of sulfonated-3’5’-diflurodiphenyl sulfone monomer, **1c**, and a non-sulfonated monomer 4,4-difluorodiphenylsulfone. The polymers had the following IEC values: 0.91, 1.10, 1.28 and 1.46 meq/g. To confirm that both monomers were successfully incorporated into the polymers DEPT 90 ^{13}C NMR spectra were acquired. An overlay of the ^{13}C DEPT 90 NMR spectrum of the homopolymer and the copolymer **2b** with an IEC of 1.46 is shown in Figure 12.

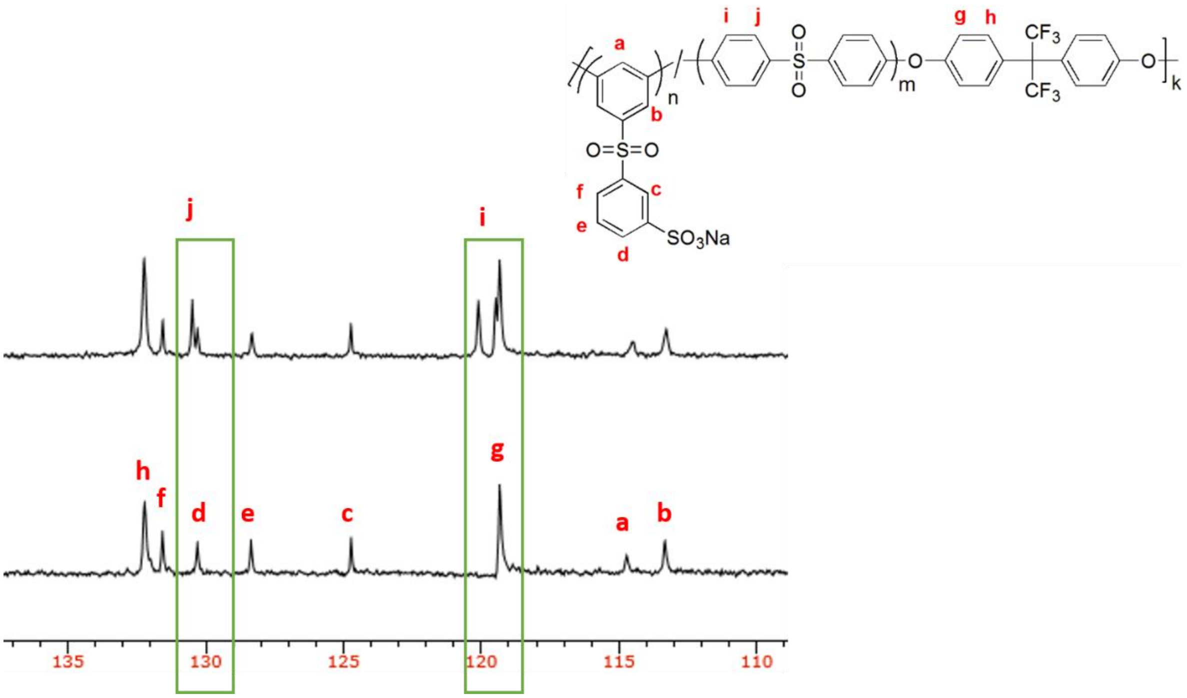


Figure 12. Overlay ^{13}C DEPT 90 NMR (DMSO-$_{d6}$) of **2a** homopolymer and **2b** copolymer.

The^{13}C DEPT 90 NMR spectrum of **2b** contains all the peaks present in homopolymer **2a,** but, as expected, has two additional signals that represent the CH groups **i** and **j** on the phenyl ring of non sulfonated monomer that is now incorporated in copolymer. In addition, the peak assigned to carbon atom **g** is showing evidence of two different magnetic environments which would result from being adjacent to the two different types of incorporated monomers.

Thermal analysis data on all polymers **2a-e** (in the salt form) was acquired using thermo gravimetric analysis (TGA) and differential scanning calorimetry (DSC). The degradation temperature for 5 % weight loss ($T_{d5\%}$) under nitrogen was determined using TGA. As shown in Figure 13 polymers **2a-e** were stable above 400 °C. The first degradation step is presumably due to the loss of the sulfonate group followed by the second step, which is due to the degradation of the backbone.

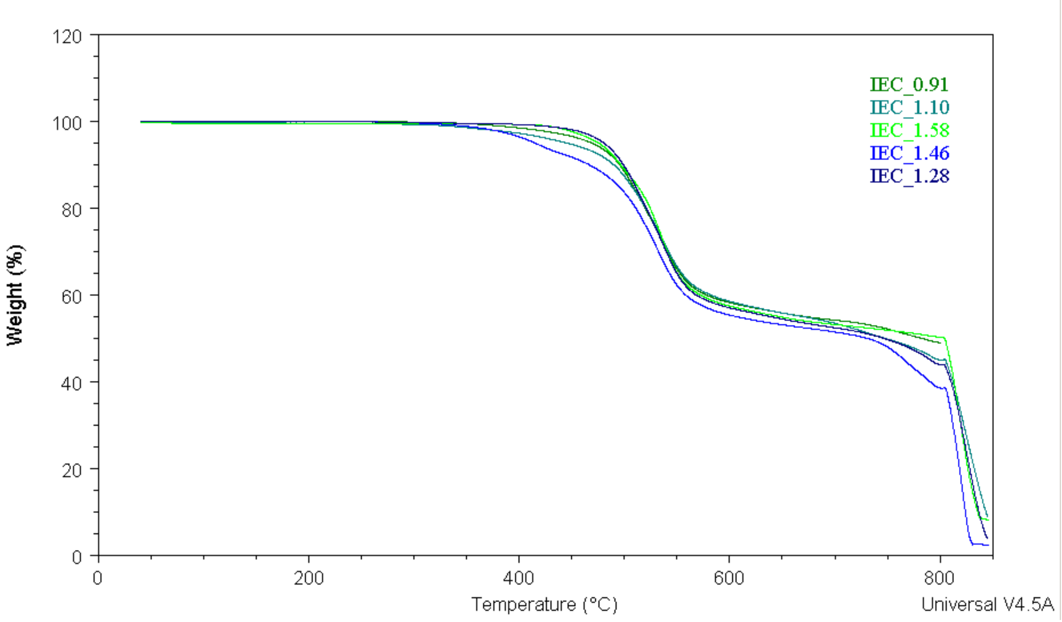


Figure 13.TGA traces of **2a-e** under nitrogen.

The T_g values of the polymers in the salt form were determined using DSC and an overlay is shown in Figure 14. All polymers had T_g values above 240 °C. The highest T_g

value was for homopolymer **2a**, 280 °C, due to the highest amount of salt present that increased inter- and intramolecular forces and decreased the ease of rotation around sigma bonds. All of the thermal data for the polymers is summarized in Table 1.

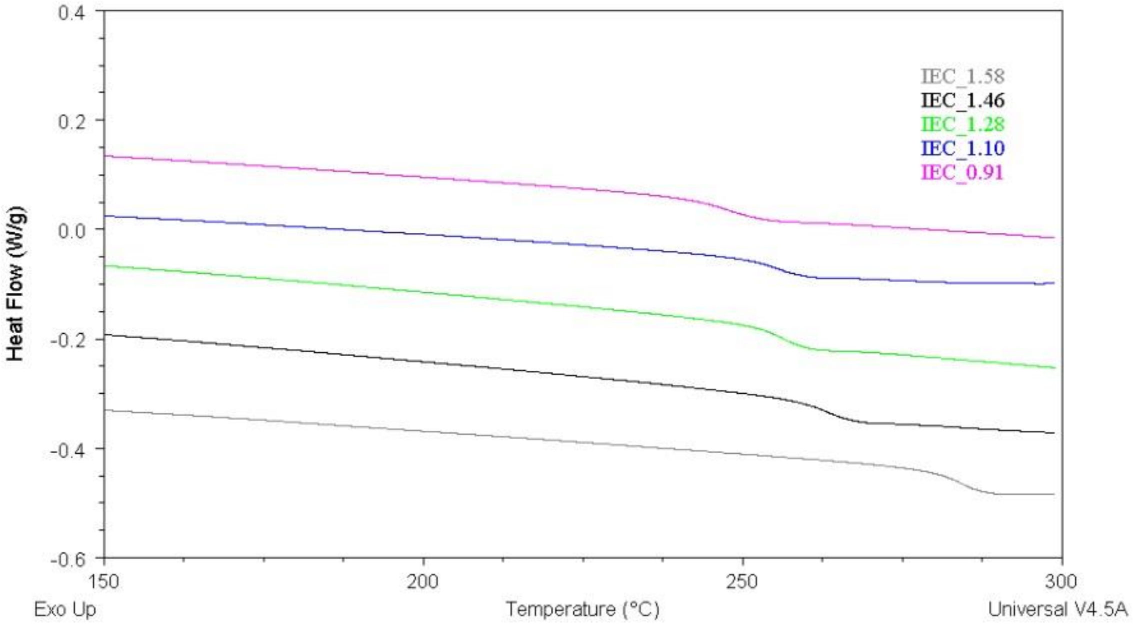


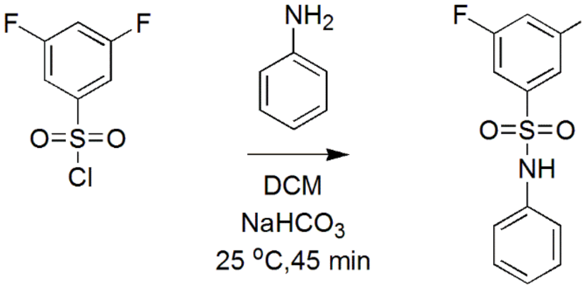
Figure 14. DSC traces of salt forms of **2a-e** in nitrogen at a heating rate of 10 °C/min.

Table 1. Thermal data of salt form of **2a-e.**

Polymer (IEC meq/g)	**$T_{d5\%}$ (°C)**	**T_g (°C)**
2a (1.58)	469	280
2b (0.91)	426	261
2c (1.10)	454	253
2d (1.28)	480	251
2e (1.46)	445	247

3.4. Synthesis of *N*-phenyl-3,5-difluoro benzene sulfonamide, 3a

A series of Bisphenol A based PAEs with a *meta* activating sulfonamide group were synthesized to explore the effects of the different alkyl chain lengths on the glass transition temperatures. As such, a series of *N*-alkyl-*N*-phenyl-3,5-diflurobenzene sulfonamides were prepared from *N*-phenyl-3,5-diflurorobenzene sulfonamide, **3a,** which was prepared as shown in Scheme **12.** Reaction of commercially available 3,5-difluorobenzenesulfonyl chloride with aniline in DCM at room temperature for 45 min afforded the desired product.



3a

Scheme 12. Synthesis of *N*-phenyl-3,5-difluoro benzene sulfonamide monomer, **3a.**

The monomer was isolated, recrystallized from ethanol /water and dried to afford **3a** in 66 % yield. The structure was confirmed by GC/MS and proton NMR spectroscopy as shown in Figure 15. In the ^{1}H NMR spectrum of monomer **3a**, signal **a** is assigned to the H on the upper phenyl ring between the two fluorine atoms and is shown as triplet of triplets due to the coupling with two fluorines with equal coupling constants ($^3J_{H\text{-}F}$ = 8.44 Hz) and two protons with the equal coupling constants ($^4J_{H\text{-}H}$ = 2.31 Hz). Proton **c** is a singlet at 6.8 ppm and it represents the proton next to the nitrogen. Protons **b**, **d**, **e**, **f** all appear as complex mutilpets between 7.11 - 7.35 ppm.

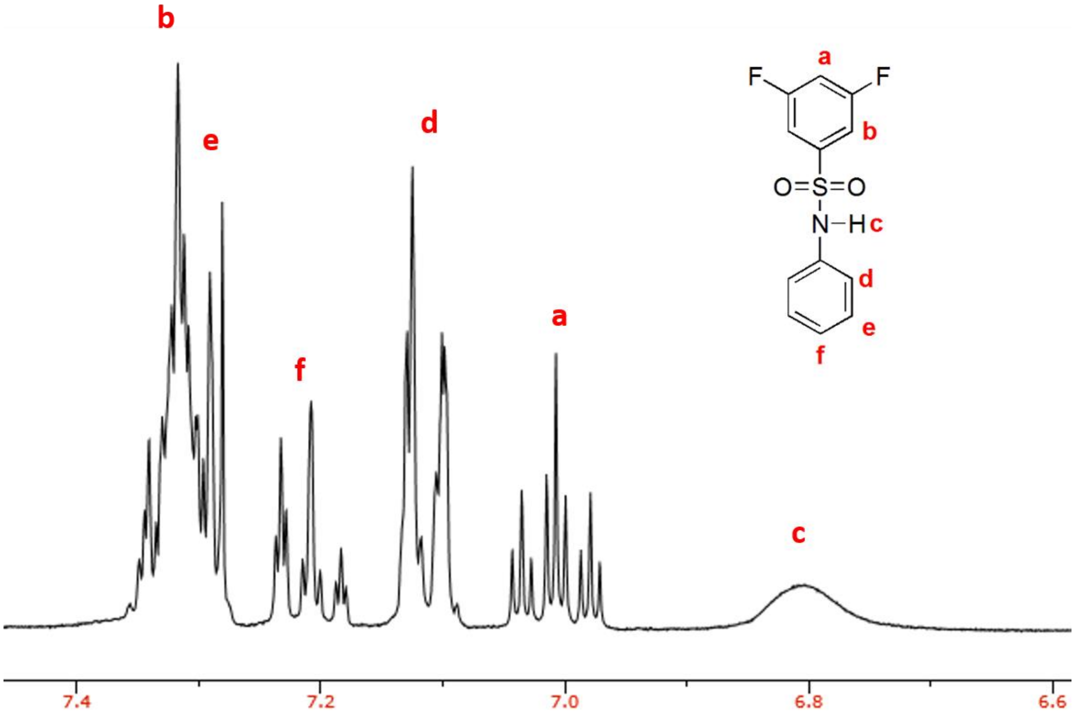


Figure 15. 300 MHz ^{1}H NMR spectrum ($CDCl_3$) of **3a.**

In the ^{13}C NMR spectrum (Figure 16) of monomer **3a**, 8 different signals are present. A triplet at 108.6 ppm represents carbon **a,** coupled with two equivalent fluorines. Carbon **b,** at 162.6 ppm and carbon **c,** at 110.6 ppm both appear as a doublet of doublets due to the coupling with fluorines. Carbon **d** is triplet at 142.1 ppm and carbons **e, g, f, h** are singlets at 135.4 ppm, 129.5 ppm, 126.2 ppm and 122.2 ppm, respectively.

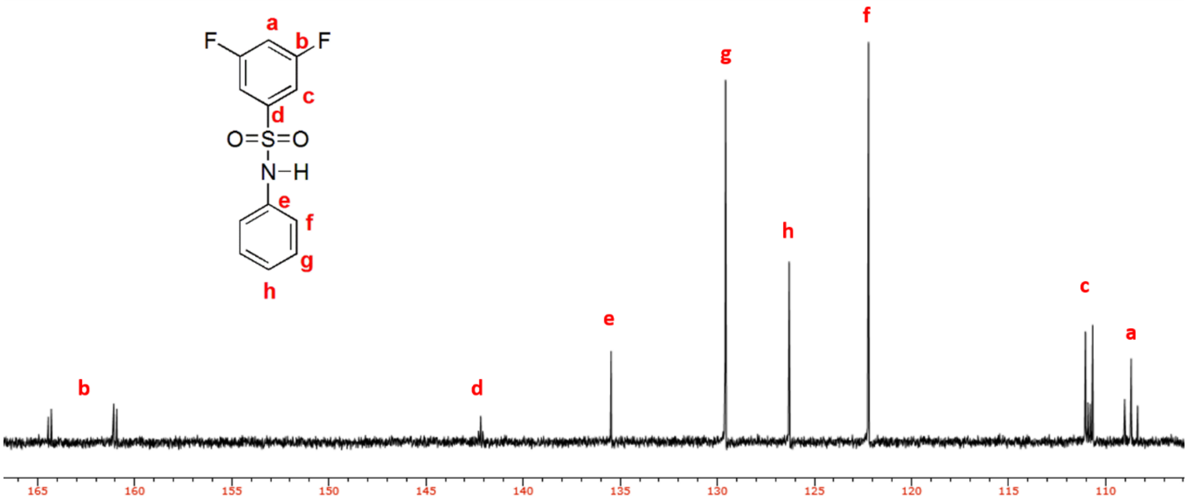
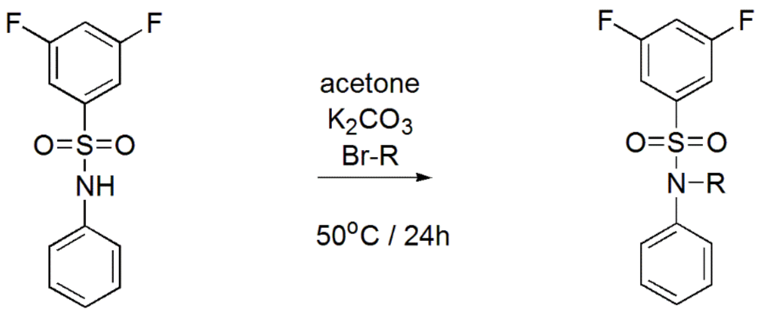


Figure 16. 75.5 MHz ^{13}C NMR (CDCl$_3$) spectrum of **3a.**

3.5 *N*-alkyl-*N*-phenyl-3,5-diflurobenzene sulfonamide derivatives, 4a-f



3a **4a-f**

R = C_3H_7, C_4H_9, C_7H_{15}, C_8H_{17}, $C_{11}H_{25}$, $C_{12}H_{27}$

(4a) **(4b)** **(4c)** **(4d)** **(4e)** **(4f)**

Scheme 13. Synthesis of *N*-alkyl-*N*-phenyl-3,5-diflurobenzene sulfonamides, **4a-f.**

The synthesis of *N*-alkyl-*N*-phenyl derivatives was achieved by alkylation of **3a** with bromoalkanes containing different chain lengths, from 3 to 12 C atoms as shown in Scheme 13. Potassium carbonate was used to deprotonate monomer **3a** creating a suitable nucleophile that can be utilized in S_N2 reactions of the bromoalkanes. The reaction mixtures were heated to 50 °C for 24 h at which point the reaction mixtures were diluted with chloroform, washed with water and then isolated from organic layer by evaporating the chloroform. All of the monomers were purified by recrystallization from ethanol/water. The structures of all 6 monomers were confirmed by GC/MS, elemental analysis, as well as ^{1}H and ^{13}C NMR spectroscopy. A representative ^{1}H spectrum of monomer **4a** is shown in Figure 17. Proton **a** appears as a triplet of triplets at 7.03 ppm due to the coupling with two *ortho* fluorines ($^3J_{H\text{-}F}$ = 2.33 Hz). Proton **b** appears as a multiplet at 7.35 ppm due to the coupling with two fluorines, protons **c**, **d** and **e** appear as complex multiplets between 7.1 and 7.2 ppm. Protons **f** and **h** appear as triplets at 3.56 ppm ($^3J_{H\text{-}H}$ = 7.10 Hz) and 0.96 ppm ($^3J_{H\text{-}H}$ = 7.36 Hz) respectively, while proton **g** appears as multiplet at 1.47 ppm due to the coupling with 5 neighboring protons ($^3J_{H\text{-}H}$ = 7.16 Hz, $^3J_{H\text{-}H}$ = 7.32 Hz).

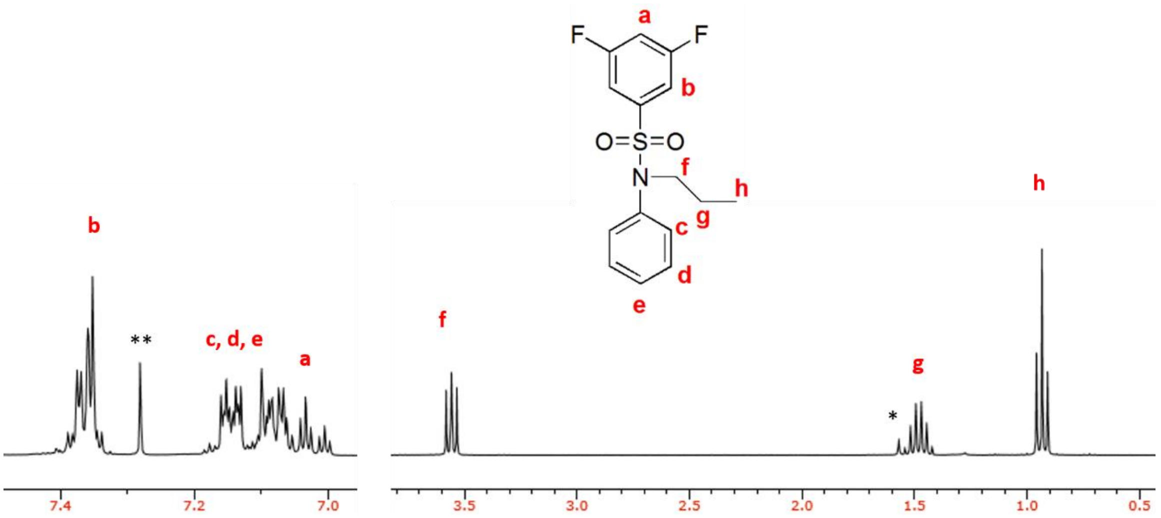


Figure 17. 300 MHz ^{1}H NMR spectrum ($CDCl_3$) of *N*-propyl-*N*-phenyl monomer, **4a.** (**$CDCl_3$,*H_2O)

A representative ^{13}C NMR spectrum for the *N*-propyl-*N*-phenyl monomer is shown in Figure 18.

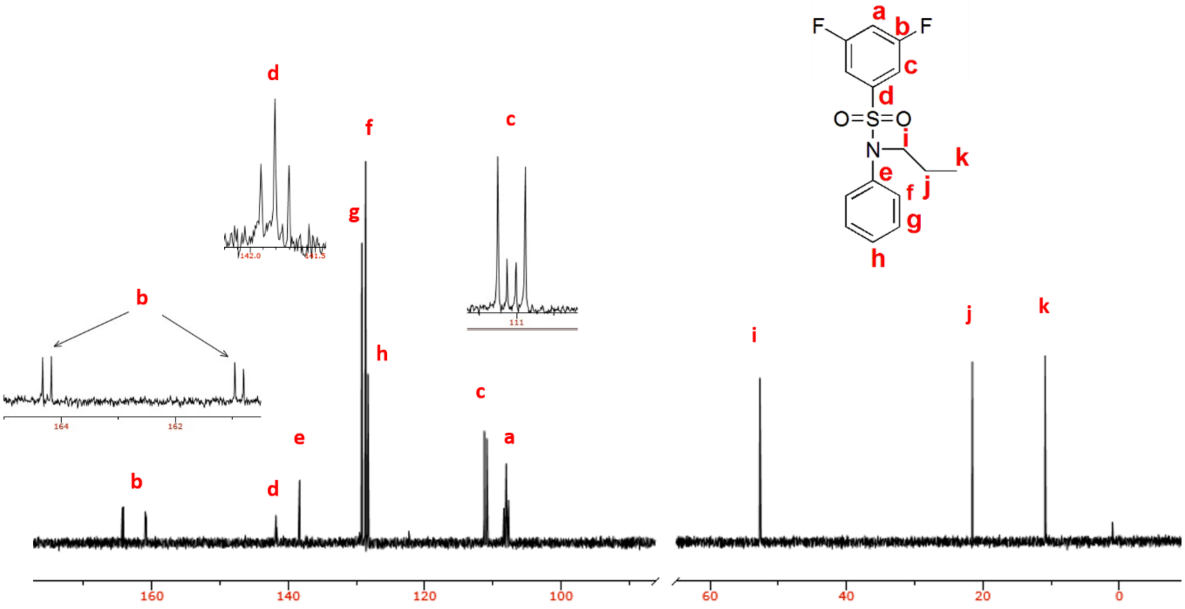
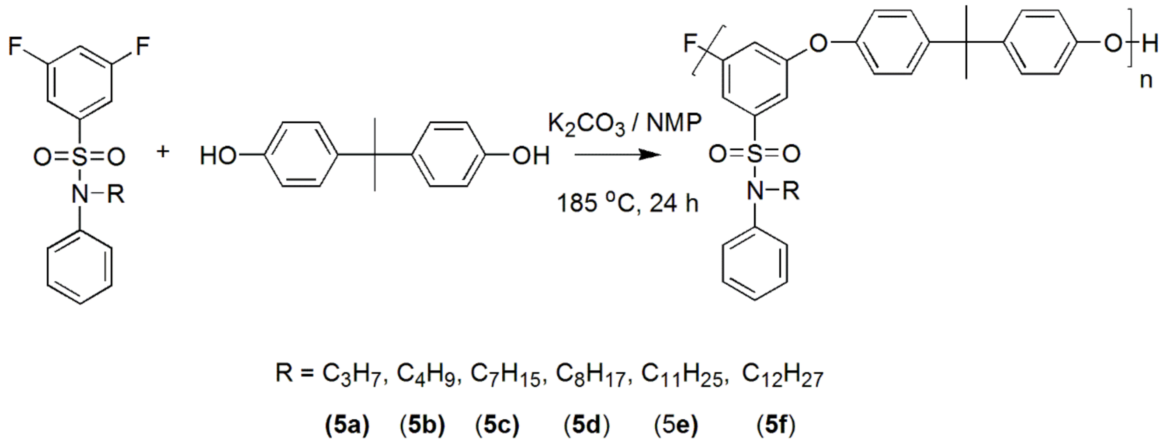


Figure 18. 75.5 MHz ^{13}C NMR ($CDCl_3$) spectrum of monomer **4a**.

The ^{13}C NMR spectrum of **4a** displays 11 distinct signals. Carbons **a-d** are shown as multiplets due to splitting by two fluorine atoms. Carbon atom **a** appears as a triplet at 107 ppm due to the coupling with two equivalent fluorines ($^{2}J_{C\text{-}F}$ = 25.04 Hz). Carbons **b** and **c** appear as doublet of doublets at 160-164 ppm ($^{1}J_{C\text{-}F}$ = 254.27 Hz; $^{3}J_{C\text{-}F}$ = 11.55 Hz) and 110-111 ppm ($^{2}J_{C\text{-}F}$ = 18.42 Hz; $^{4}J_{C\text{-}F}$ = 9.33 Hz), respectively, due to the coupling with two fluorine atoms. Carbon **d,** coupled with two *meta* fluorines**,** is a triplet at 141 ppm ($^{3}J_{C\text{-}F}$ = 8.17 Hz). Carbons **e-f** on the bottom phenyl ring, all give rise to singlets. Carbon **e** appears at 138 ppm, followed by carbon **g** at 129 ppm, **f** at 128.6 and 128.3 for carbon **h.** Due to the inductive effect carbon **g** appears more downfield than carbon **f.** The remaining three signals are for carbon atoms **i, j** and **k** on the alkyl chain and they appear far upfield as singlets at 30.9 ppm, 21.5 ppm and 10.9 ppm respectively.

3.5. Polymerization of 4a-f (*N*-alkyl-*N*-sulfonamide) with Bisphenol A

The Bisphenol A based PAEs, from monomers **4a-f**, were prepared via NAS polycondensation which was carried out at 185 °C for 24 h in the presence of potassium carbonate as a proton trap (Scheme 14).



Scheme 14. Synthesis of sulfonamide based PAEs, **5a-f**

The polymers were precipitated from water, isolated via vacuum filtration and dried. In oreder to determine if any cyclic species were present, all of the polymers were analyzed by Size Exclusion Chromatography, SEC, which indicated the presence of some low molecular, presumably, cyclic material. To remove any cyclics, the polymers were dissolved in chloroform and reprecipitated from isopropanol and the resulting solids were isolated via filtration. Analysis by again by SEC confirmed the removal of cyclics as shown by the SEC traces of sample of **5c** in Figure 19.

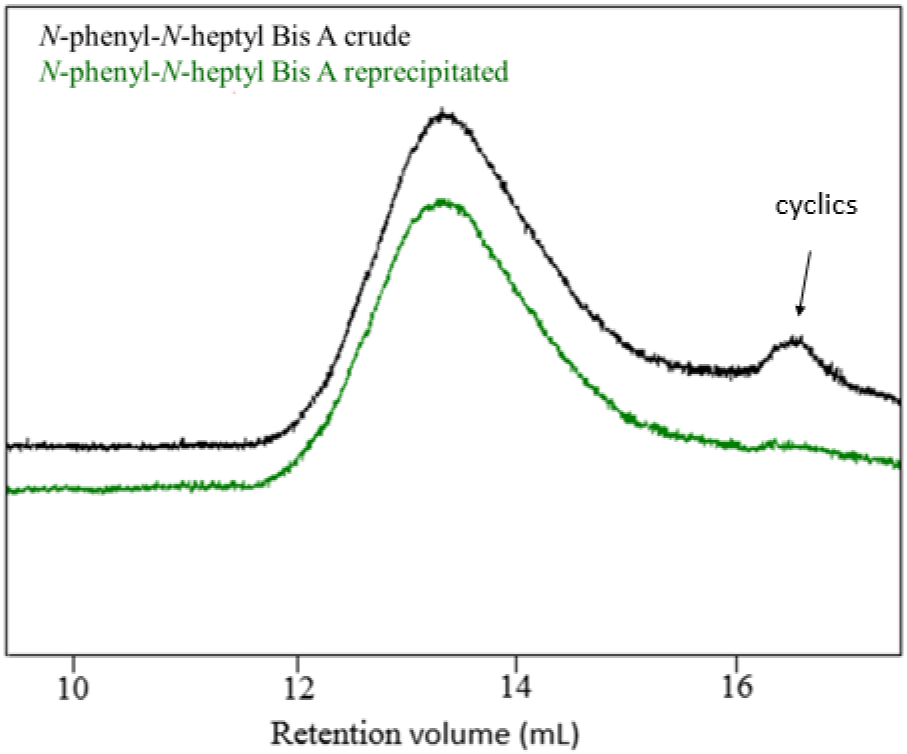


Figure 19. SEC traces of crude and reprecipitated **5c** polymer.

SEC was done with polymers soluble in 5% acetic acid/THF mixture. Weight average molecular weights M_w, number average molecular weights M_n and polydispersity index values were determined using the light scattering and refractive index detectors. Molecular weight and PDI values for all polymers are listed in Table 2.The polymers had sufficiently high molecular weights from 23,500 Da for **5a** to 78,000 Da for **5f**, to promote chain entanglements and the preparation of polymer films. Polydispersity index values were determined using a conventional calibration and ranged from 1.8 for **5d** to 2.3 for **5f.**

Table 2. Molecular weight data, PDI values and % yields of **5a-f.**

Polymer	**% yield[a]**	**M_w (Da)**	**PDI**
5a	74	23,500	2.18
5b	70	38,500	2.00
5c	69	42,700	1.92
5d	70	32,500	1.88
5e	80	80,500	2.13
5f	72	78,000	2.34

[a]. after reprecipitation from isopropanol.

To confirm the polymer structures ^1H and ^{13}C NMR spectroscopy was performed on all of the samples. The ^{13}C NMR spectrum of **5b** is shown in Figure 20 and confirms that the polycondenasation reaction led to the targeted polymers. Carbon **a-d** in the monomer ^{13}C NMR spectrum all gave rise to multiplets due to the coupling with *meta* fluorines. Upon displacement of the fluorines in the polymerization reaction with Bisphenol A all of the multiplets now collapsed to singlets. Carbon atom **a,** which appeared as a triplet at 107 ppm in the fluorinated monomer, is now present as a singlet at 112.2 ppm. Carbon **d,** also a triplet in the monomer unit at 141.8 ppm is now a single peak at 140.6 ppm. Carbons **b** at 162.5 ppm and **c** at 111.0 ppm in the fluorinated monomer, previously appearing as doublet of doublets, now collapsed to singlets at 159.1 ppm and 111.0 ppm respectively. Four additional signals are present in the aromatic region for carbons **n, m, o** and **p** at 119.0, 128.3, 151.5, 152.4 ppm respectively, as well as two new signals in alkyl region, **q** at 42.3 ppm and **r** 30.9 ppm, that arise from Bisphenol A. In the alkyl region, singlets **i**, **j**, **k**, **l** at 50.4, 30.2, 19.5 and 13.5 ppm represent carbons on pendent butyl group.

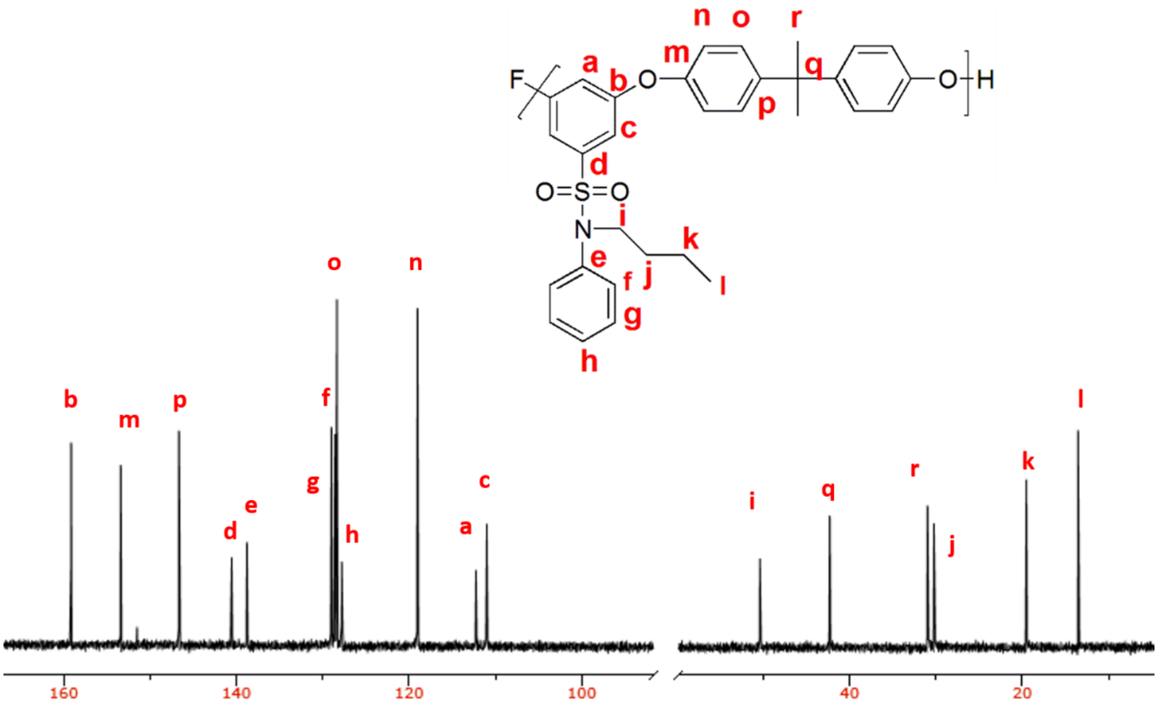


Figure 20. 75.5 MHz ^{13}C NMR (CDCl$_3$) spectrum of polymer **5b**.

The thermal properties of the polymers were examined by Thermogravimetric analysis (TGA) and Differentials Scanning Calorimetry (DSC). All of the polymers had high thermal stability above 350 °C, in nitrogen atmosphere, and degraded in two distinct steps. The onset temperature for first degradation step was from 359° C **5c** for to 370°C for **5a.**

The TGA thermogram of polymer **5e,** under nitrogen is shown in Figure 21, and it clearly shows the two degradation steps.

. The first degradation step is attributed to the loss of the *N*-phenyl-*N*-alkyl moiety. The theoretical percentage weight loss values calculated based on the ratio of *N*-phenyl-*N*-alkyl moiety to the repeat unit were close to the experimental values (see Table 3). For example, the calculated percent weight loss for the *N*-undecyl-*N*-phenyl group was 41.3 % while the observed value was 40.2 %. Loss of the entire sulfonamide group in the first step was ruled out due to the poor agreement in the calculated and experimental values. For example with the *N*-undecyl-*N*-phenyl polymer, **5e**, the theoretical value was 50.7 % while the observed value was only 41.3 %. The TGA data for the first degradation step for all the polymers are listed in the Table 3 together with calculated weight loss percentages.

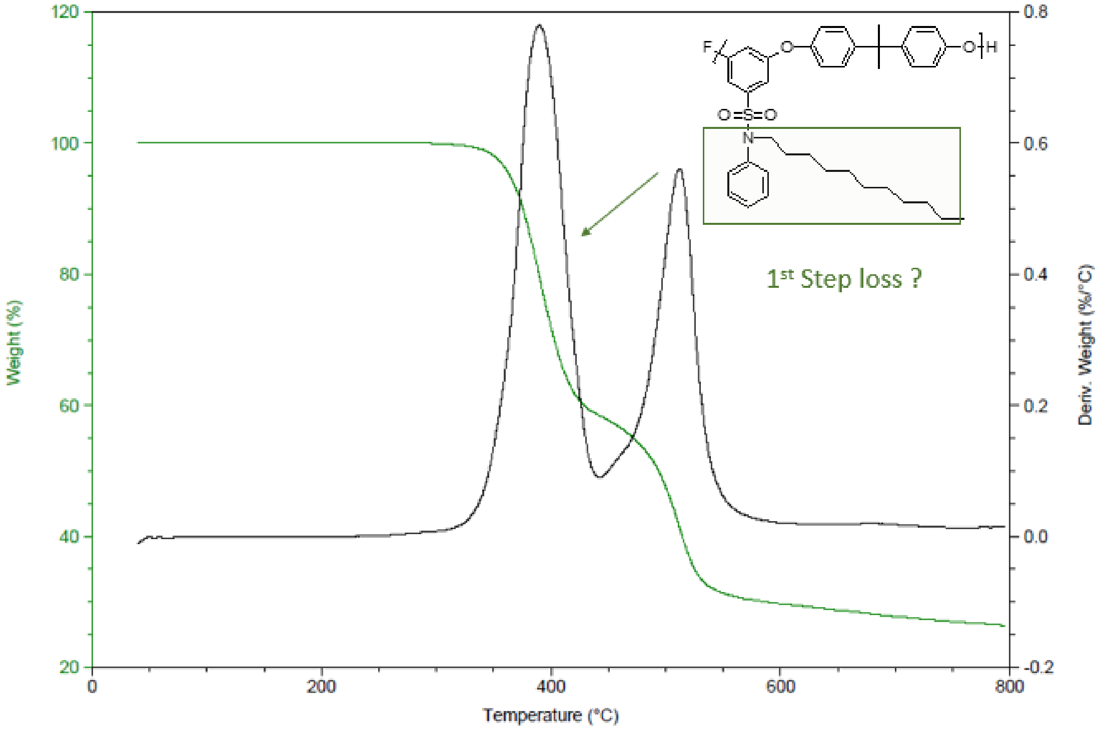


Figure 21. TGA trace of *N*-undecyl-*N*-phenyl, **5e** under nitrogen.

Table 3. Thermogravimetric analysis of *N*-alkyl-*N*-phenyl sulfonamides.

Polymer	**$T_{d\ onset}$ (N_2) 1st Step (°C)**	**1st Step % loss observed**	**Weight % *N*-PhR**	**Weight % SO_2*N*-PhR**
5a	370	29.9	26.8	46.1
5b	368	31.6	28.8	41.3
5c	359	36.5	34.2	45..7
5d	359	38.8	35.8	47.1
5e	361	41.3	40.2	50.7
5f	364	41.8	41.6	51.8

The second degradation step under nitrogen may be related to the loss of a phenyl and sulfone moiety with possible loss of oxygen from Bisphenol A as well. The observed percentage weight losses, based on the ratio of the phenyl sulfone moiety to weight of repeat unit, have relatively close values to the calculated ones. For example the observed percent loss for the second degradation step for *N*-undecyl-*N*-phenyl polymer, **5e,** is 28.8 %, while the calculated value for phenyl-sulfone moiety is 22.7 % without oxygen and 25.3 % with oxygen. Values for the percentage weight loss for the second degradation step are summarized in Table 4.

Table 4. TGA analysis data for the 2nd degradation step.

Polymer	**2st Step %(N_2) loss observed**	**Weight % SO_2Ph**	**Weight % SO_2Ph-O-**
5a	29.4	27.8	31
5b	29.3	27.0	30.2
5c	31.6	25	27.9
5d	24.4	24.4	27.3
5e	28.8	22.7	25.3
5f	28.5	22.2	24.8

Differential Scanning Calorimetry (DSC) was used to measure the glass transition temperatures (T_g) of the prepared polymers. An overlay of the DSC traces of all six polymers is shown in Figure 22. The traces indicate that the polymers synthesized were completely amorphous since only glass transition temperatures observed with no other thermal transitions, such as melting point or crystallization temperatures. The T_g is determined a measure of the ease of motions in the polymer backbone via rotations around sigma bonds. Higher glass transition temperatures are attributed to the polymers that have less segmental motion and less free volume for those motions to occur.

The T_g of all the polymers decreased gradually with an increased length of the alkyl chains, starting from polymer **5a** with a T_g of 111 °C to **5f** with a T_g of 46 °C. With a short alkyl chain, such as propyl, attached to the monomers as in the **5a** polymer, the T_g of 111

°C is relatively high, indicating that rotations in the polymer are limited due to the lower free volume provided for the polymers segments to rotate around sigma bonds. As the length of alkyl chain is increased by one CH_2 group the steric hindrance should increase, which would contribute to a higher glass transition temperature, however the T_g observed decreased to 103 °C. This decrease may be due to an increase in free volume between polymer chains and thus increased ease of chain rotations. Similar changes are observed in poly(acrylates) and poly(methacrylates)s as described in section 1.2.

Polymers **5c** and **5d**, with heptyl and octyl pendent groups, had even lower T_g values of 74 °C and 66 °C, respectively. With a further increase of alkyl chain length to undecyl and dodecyl, the T_g values dropped significantly to 52 °C for **5e** and 46 °C for **5f**. Pendent long alkyl chains have contributed to higher molecular masses but also have provided more free volume for segmental motions in polymers and have decreased the glass transition temperatures.

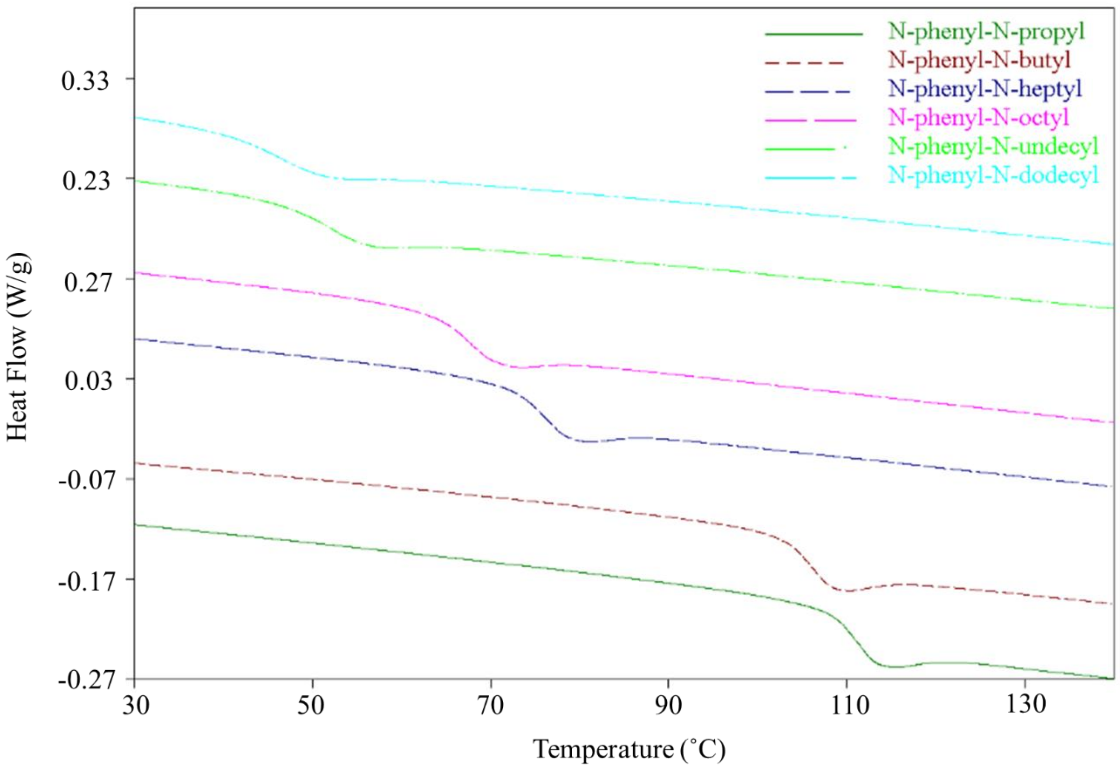


Figure 22. DSC traces of *N*-alkyl-*N*-phenyl polymers in nitrogen at a heating rate of 10°C/min.

4. CONCLUSION

A series of sulfonated PAE with varying IEC has been prepared. In order to tune IEC values, different ratios of sulfonated and non-sulfonated monomer were employed. Fully sulfonated homopolymer, **2a,** with an IEC of 1.58 meq/g was prepared using monomer **1c** and Bisphenol AF. Copolymers were prepared with varying ratios of monomer to achieve IEC values from 0.91 as the value of the currently used Nafion®, to IEC values of 1.10, 1.28 and 1.46. Incorporation of both monomers was confirmed by ^{1}H and ^{13}C NMR spectroscopy. The polymers were prepared in salt form, so they must be converted to the acid form prior to further thermal analysis and proton conductivity measurement, which are required to fully evaluate them as potential candidates for PEMs.

A series of sulfonamide based PAE, **5a-f**, derived from Bisphenol A and *N*-phenyl-3,5-difluoro benzene sulfonamides has been synthesized via NAS. The effect of alkyl chain length on polymer thermal properties has been determined.

The molecular weight and PDI values were determined by SEC analysis. All 6 polymers, **5a-5f**, had sufficiently high molecular weights from 23,500 Da for **5a** to 78,000 Da for **5f**, to allow chain entanglements and the casting of flexible films. As analyzed by TGA, the polymers were all completely amorphous and had relatively high thermal stability with onset degradation temperatures above 350 °C. The glass transition temperatures were tuned utilizing different lengths of alkyl chains. As expected, the PAE with the shortest pendent alkyl chain, **5a,** had the highest T_g value of 111 °C, due to less free volume for segmental motions to occur. As the length of alkyl chain increased from butyl in **5b** to dodecyl in **5f,** the T_g decreased from 103 °C to 46 °C. Longer alkyl chains have provided more free volume between polymers chain and allowed the polymer chains segments to rotate more easily, thus decreasing glass transition temperatures.

5. FUTURE WORK

In order to fully develop the new sulfonated PAEs as potential candidates for PEMs, conversion to acid form and full characterization is needed. Once converted to the acid forms, films should be made and proton conductivity data obtained.

Sulfonamide based PAEs have been fully characterized, but there is still the possibility to synthesize PAEs functionalized with alkyl chain lengths in between to complete the series of PAEs or even longer chains to determine when the intermolecular forces of the side chain begin to reverse the trend and increase the T_g. Since the alkyl chains shown the effect on glass transition temperature with relatively high thermal stability there is a potential to use the sulfonamide based PAEs as high temperature elastomers. However for use as elastomers, the polymers must be crosslinked so there is an interest to synthesize copolymers with crosslinkable groups such as allyl or propynyl.

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