2015

Tuning the Physical Properties of Poly(arylene ether)s Prepared from 3,5-Difluorobenzene Sulfonamides

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TUNING THE PHYSICAL PROPERTIES OF POLY(ARYLENE ETHER)S PREPARED FROM 3,5-DIFLUOROBENZENE SULFONAMIDES

A thesis submitted in partial fulfillment

of the requirements for the degree of

Master of Science

By:

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B.S., University of Zagreb, 2010

2015

Wright State University

WRIGHT STATE UNIVERSITY
GRADUATE SCHOOL

June 25, 2015

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Renata Mitton ENTITLED Tuning the Physical Properties of Poly(arylene ether)s Prepared from 3,5-Difluorobenzene Sulfonamides BE ACCEPTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF Master of Science.

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ABSTRACT

Mitton, Renata. M.S., Department of Chemistry, Wright State University, 2015. Tuning the Physical Properties of Poly(arylene ether)s Prepared from 3,5-Difluorobenzene Sulfonamides

A series of functionalized poly(arylene ether)s, PAEs, based on 3,5-difluorobenzene sulfonamides with varying groups on the sulfonamide moiety were investigated. The main goal of the project was to tune the physical properties of the PAEs by altering the organic groups present on the sulfonamide nitrogen atom, including combinations of aryl iodide, alkyl, allyl, 4-ethoxycarboxylphenyl and benzyl moieties.

Using 3,5-difluorobenzenesulfonyl chloride as a starting material, *N*-R_1-*N*-R_2-3,5-difluorobenzenesulfonamides were prepared, followed by conversion to the corresponding PAEs by reaction of 3,5-difluorobenzene sulfonamides with Bisphenol-A, via a typical NAS polycondensation. Copolymers with varying contents of the functional monomer ranging from 10 to 25 %, were prepared using 4,4`-difluorodiphenylsulphone as the comonomer.

The polymers were characterized by size exclusion chromatography (SEC), NMR spectroscopy, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The polymers displayed moderate thermal stability in air while the glass transition temperatures depended on the structure of the R groups.

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ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to my advisor, Dr. Eric Fossum for his guidance, support and patience during the masters program. I am very thankful to my committee members Dr. William Feld and Dr. Daniel Ketcha for their suggestions towards this thesis. I would also like to thank the past and present members of the Fossum research group, as well as the faculty and staff members of the Wright State University Department of Chemistry.

This material is based upon work supported by the National Science Foundation under CHE-1307117.

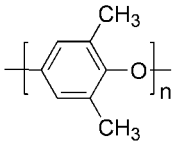
DEDICATION

I would like to dedicate this thesis to my parents, Elsa and Ennio Mitton, who have sacrificed so much of their own lives to give me the opportunity to earn a higher education. I would also like to give my special thanks to my sisters and friends for their continuous love and support.

1. INTRODUCTION

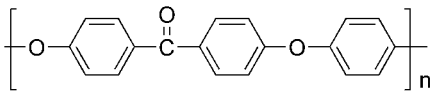
1.1. Poly(arylene ether)s PAEs

Poly(arylene ether)s, PAEs are a class of high performance engineering thermoplastics which can be recognized by aromatic rings linked by ether bonds. High performance thermoplastics are receiving considerable attention for their applications in aerospace, automotive, electronic and related markets.[1] Having good mechanical properties, excellent thermal stability, high glass transition temperatures (T_g), resistance to oxidation and hydrolysis makes them widely used in a variety of industrial applications such as coatings, adhesives, composites, molded components, toughening agents and ultrafiltration membranes. The structures of some common, commercially available poly(arylene ethers), PAE, include poly(2,6-dimethylphenylene oxide), **PPO**, poly(ether ether ketone), **PEEK**, and poly(arylene ether sulfone), **PAES**, are shown in **Figure 1**. PAEs are mainly synthesized by nucleophilic aromatic substitution of activated aromatic halides or via Friedel-Crafts processes.[2]



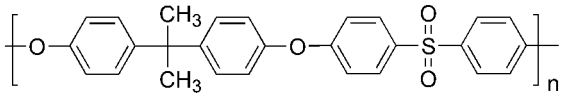
Poly(phenylene oxide), **PPO**

T_g = 208 °C ; T_m= n/o



Poly(ether ether ketone), **PEEK**

T_g = 143 °C ; T_m = 343 °C



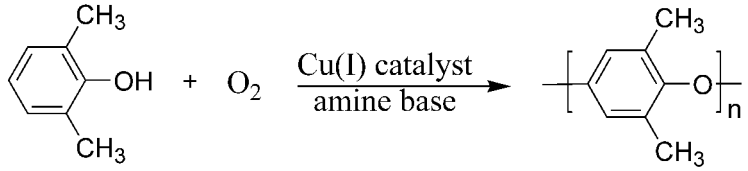
Poly(arylene ether sulfone), **PAES**

T_g= 190 °C ; T_m= n/o

Figure 1. Structures of some common commercially available PAEs.

1.1.1. Poly(phenylene oxide) PPO

Poly(2,6-dimethyl-1,4-phenylene oxide), **PPO**, a poly(phenylene ether), is an important engineering thermoplastic synthesized by oxidative coupling. The process involves passing oxygen through a vigorously stirred 2,6-dimethylphenol solution in the presence of a copper catalyst and an amine base, as illustrated in **Scheme 1**.



2,6-dimethylphenol poly(2, 6-dimethylphenylene oxide), **PPO**

Scheme 1. Synthetic route to PPO.

Owing to excellent physical properties, stiffness, tensile strength, a high glass transition temperature of 208 ^{o}C, as well as resistance to oxidizing agents and low water absorption, **PPO** has found use in a variety of applications such as the automotive industry, electronics areas, business machines, and gas separation membranes. However, the high price of **PPO** has restricted its application and led to introduction of the related and cheaper thermoplastic materials by General Electric under the trade name Noryl®, which is a blend of **PPO** and polystyrene.[1]

1.1.2. Poly(ether ether ketone) PEEK

Many aromatic poly(ether ketone)s are semi-crystalline high performance thermoplastics, which include structures that contain aromatic rings linked by ether bridges and ketone moieties in the backbone. Some of the common poly(aryl ether ketone)s are shown in **Figure 2** and include poly(ether ketone), **PEK**, poly(ether ketone ketone), **PEKK**, and poly(ether ether ketone), **PEEK** as well as other combinations. Due to the aromaticity of their backbone they all exhibit high thermal stability and excellent mechanical properties, as well as chemical resistance, which makes them commercially attractive materials.[3]

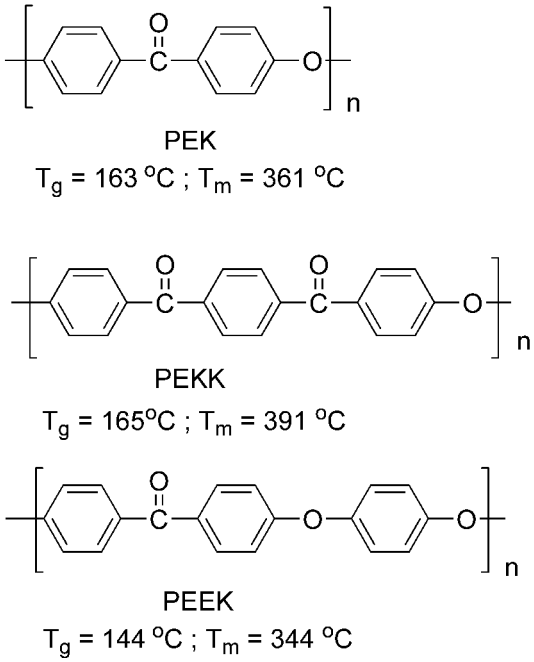
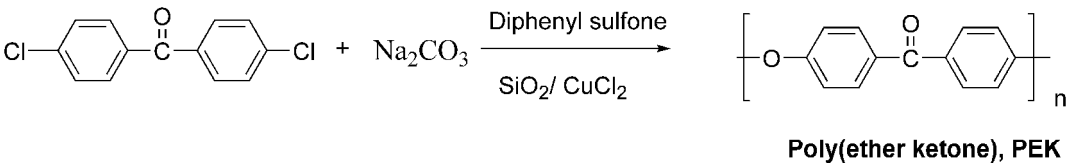


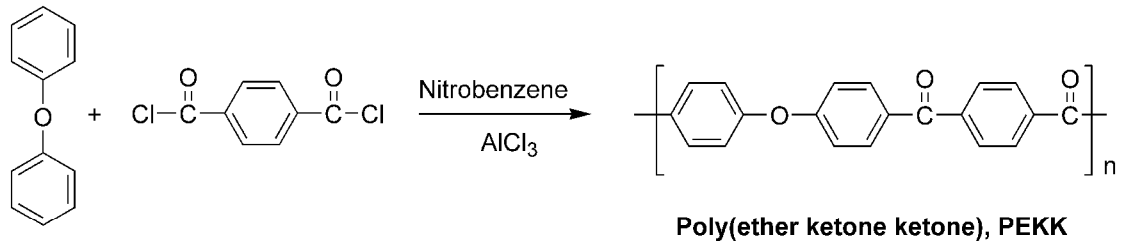
Figure 2. Structures of PEK, PEKK, PEEK.

The first synthesis of poly(ether ketone) via NAS of an activated non-fluoro monomer was described by Fukawa *et al*[4] using 4,4'-dichlorobenzophenone. The polymerization reaction was carried out in diphenyl sulphone at high temperatures (280-320 °C) in the presence of Na_2CO_3 and $SiO_2/CuCl_2$ catalyst as shown in **Scheme 2**. The product was washed with an aqueous NaOH solution removing the silicon dioxide. The intermediate formed between the 4,4'-dichlorobenzophenone and the silanol on the surface of the silica was proposed to be a silyl ether.



Scheme 2. Synthesis of poly(ether ketone) via NAS.

The first synthesis of the completely aromatic poly(ether ketone ketone) was described by Bonner, in 1962. The Friedel-Crafts acylation involved a reaction between diphenyl ether and terephthaloyl chloride in nitrobenzene, using aluminum chloride as a catalyst. The reaction scheme is given below (**Scheme 3**).[5] However, due to insolubility in most organic solvents, only low molecular weight polymers were obtained.



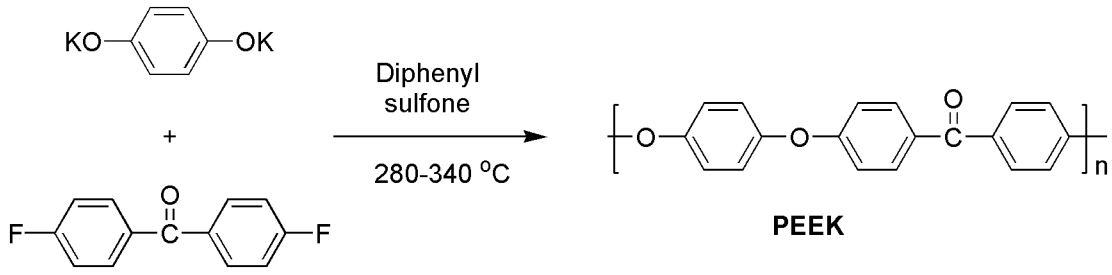
Scheme 3. Synthesis of poly(ether ketone ketone) by EAS.

PEEK is a semi-crystalline, high temperature resistant thermoplastic with a T_g of 143 °C and a melting temperature (T_m) of 343°C. The polymer exhibits low water absorption, as well as resistance to acids and bases. Typical applications of PEEK include coating and insulation for high performance wiring in aerospace and computer industries, military equipment, nuclear plant applications, oil wells.[6]

The synthesis of PEEK was first reported by Bonner[5] at Imperial Chemical Industries, ICI, in 1978 under the trade name Victrex®. It can be synthesized by two different condensation polymerization routes[7]; nucleophilic and electrophilic aromatic substitution (Friedel-Crafts acylation). The nucleophilic aromatic substitution, NAS, involves activated aryl dihalide monomers reacting with aromatic diphenolates in a polar,

aprotic solvent, while the Friedel-Crafts route involves coupling of aromatic diacyl monomers with aryl ethers.

Semi-crystalline **PEEK** is synthesized commercially by the reaction of 4,4`-difluorobenzophenone with the dipotassium salt of hydoquinone in diphenylsulphone, as shown in **Scheme 4**.[8]



Scheme 4. Synthesis of poly(ether ether ketone) via NAS.

1.1.3. Poly(arylene ether sulfone)s PAES

Poly (arylene ether sulfone)s, **PAES**, are a class of amorphous engineering thermoplastics with excellent high temperature properties, good mechanical strength, high resistance to oxidation and hydrolysis. The presence of rigid aromatic structures along with the very polar sulfonyl group give rise to relatively high glass transition temperatures, > 190 ^{o}C. Different T_g values are observed with varying the bisphenol units.

Poly(arylene ether sulfone)s are used in a variety of industrial applications requiring good temperature resistance, hydrolytic stability, including electrical appliances and components, connectors, adhesives, films, membranes.[4]

The first commercial poly(arylene ether sulfone), Udel, was introduced by Union Carbide in 1965. The structures and T_g values of some commercially available PAES are shown in **Figure 3**.

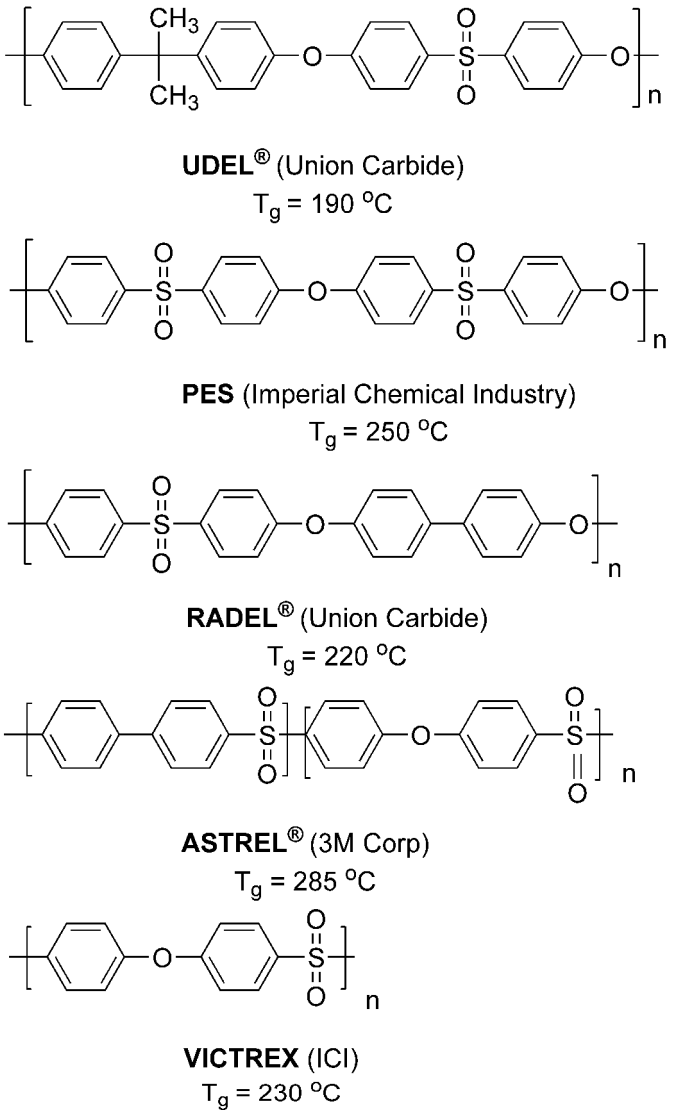
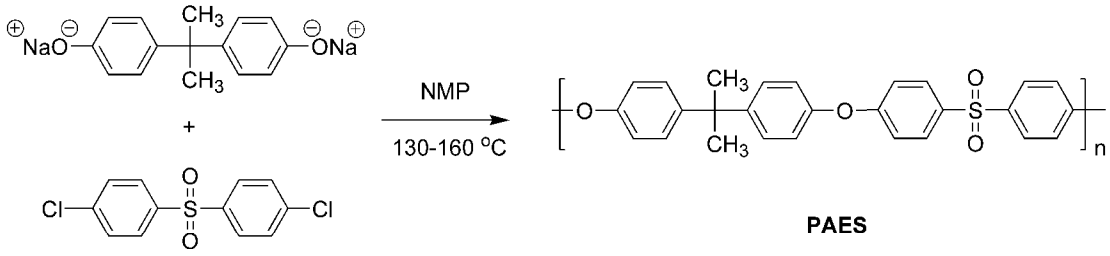


Figure 3. Commercially available PAES.

PAES can be synthesized by nucleophilic aromatic substitution, NAS, or electrophilic aromatic substitution EAS.[9, 10]

Today, the nucleophilic aromatic substitution polycondensation route is used for commercial production of these thermoplastics. The reaction between 4,4'-dichlorodiphenyl sulfone and an alkaline salt of Bisphenol-A in an aprotic solvent system such as *N*-Methyl-2-pyrrolidone, NMP or dimethyl sulfoxide, DMSO[11] gives rise to UDEL (**Scheme 5**).

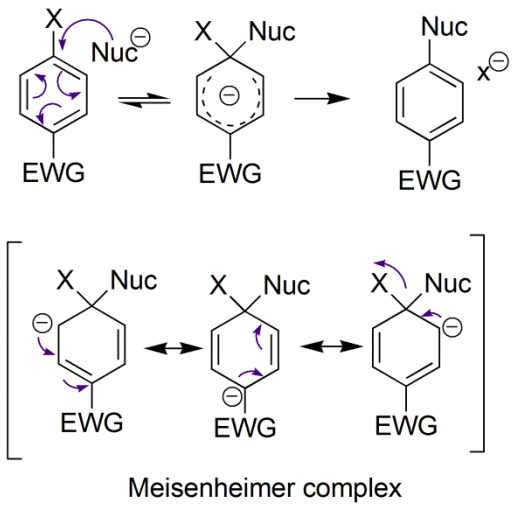


Scheme 5. Synthesis of poly(arylene ether sulfone) by NAS.

1.2. Polycondensation by Nucleophilic Aromatic Substitution NAS

Poly(arylene ether)s are commonly synthesized by nucleophilic aromatic substitution. A typical NAS mechanism involves activation of an aryl halide by an electron withdrawing group, EWG, usually a sulphonyl, carbonyl or phosphoryl group, located in the *para*-position, as shown in **Scheme 6.** The mechanism takes place in two steps; the first one is considered to be reversible and the rate determining step, a nucleophilic attack at the *ipso* carbon, resulting in a resonance stabilized intermediate known as a Meisenheimer complex. The second one involves regaining aromaticity of the benzene ring and loss of the leaving group, in this case a halide.

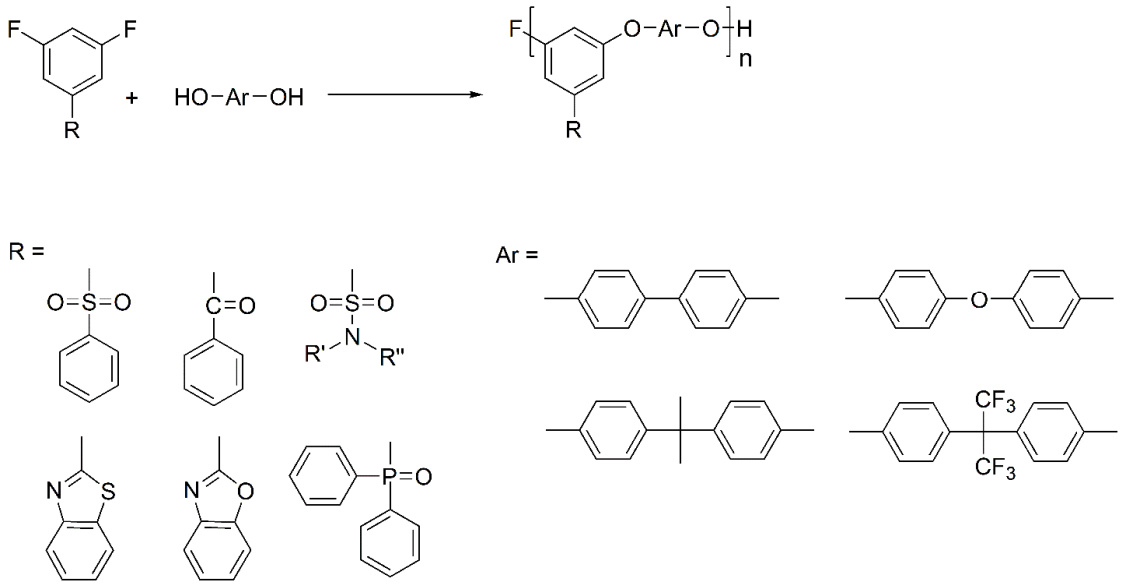
In the first step the EWG increases the reaction rate by decreasing the electron density at the *ipso* carbon, making it electrophilic, whereas an electron donating group, EDG, would have the opposite effect.



Scheme 6. Typical NAS mechanism for a *para* activated system.

Even though NAS reactions are usually carried out with the aryl halides activated by an EWG in the *ortho* or *para* position, NAS can also take place at the *meta* position relative to the EWG group.

Kaiti *et al*[12] were the first to use a 3,5-difluoro aromatic system for NAS polycondensation reactions. Since then our group has introduced a variety of activating groups for the synthesis of PAEs via the *meta* activated NAS reactions[13, 14, 15] as shown in **Scheme 7**. In these systems the activating groups reside pendent to the polymer backbone and allow introduction of functional groups without directly altering the backbone of the polymer.

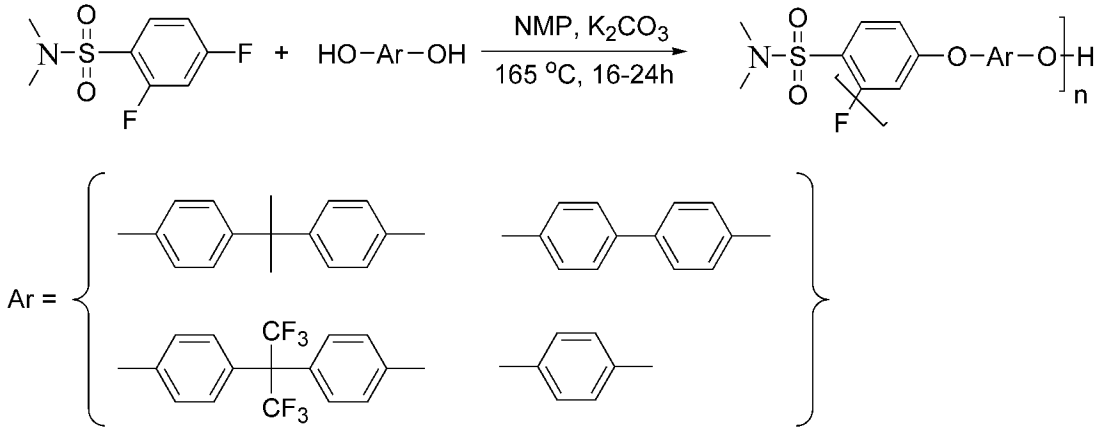


Scheme 7. Synthesis of PAE via *meta*-activated NAS polycondensation reactions.

1.3. Sulfonamides as activating groups for NAS

Sulfonamides are widely used in the pharmaceutical industry,[16] nevertheless, they have also been reported to provide activation for NAS reations.[17-21] More recently sulfonamides have been utilized as the activating group for NAS polycondensation reactions leading to PAEs.[15, 22, 23] Sulfonamides have been described as strong electron withdrawing groups for the activation of aryl halides, towards NAS reactions, in *ortho* and *para*,[22] as well as in the *meta* positions.[15, 23] They are an attractive activating group since they provide a site for introducing a variety of functional groups pendent to the polymer chain, a feature that can be exploited to tailor the properties for a specific application.

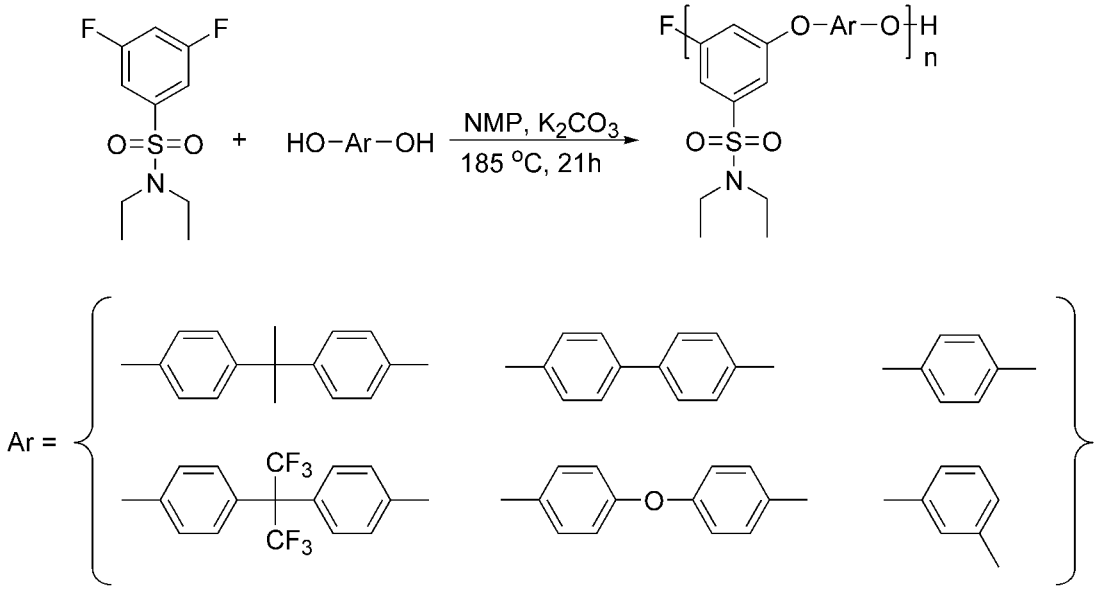
Rebeck and Knauss published a paper in 2011 in which they produced poly(aryl ether sulfonamide)s utilizing the sulfonamide moiety as a new activating group for nucleophlic aromatic substitution polymerization. The monomer, *N*,*N*-dimethyl-2,4-difluorobenzenesulfonamide, was reacted with a series of bisphenols, as shown in **Scheme 8**. The characterization data of the resulting polymers indicate the sulfonamide moiety is sufficiently electron withdrawing to activate aryl fluorides for NAS in *ortho* and *para* positions. The high molecular weight polymers (M_n = 7,170- 109,000 Da) exhibited moderate to high glass transition temperatures, ($T_{g,}$ = 163- 199 ^oC) and thermal stability ($T_{d5\%}$ = 398-442 ^oC).[22]



Scheme 8. NAS polycondensation activated from the *ortho/para* positioned sulfonamide.

Our group has synthesized a series of PAEs carrying a pendant diethyl sulfonamide group prepared by the *meta* activated NAS reaction of *N*,*N*-diethyl-3,5-difluorobenzenesulfonamide with a series of bisphenols, as shown in **Scheme 9**. Characterization data indicated that the fluoride atoms were sufficiently activated by the sulfonamide group, located in the *meta* position, to provide access to high molecular

weight polymers (M_n = 6,300- 85,500 Da). The sulfonamide based PAEs displayed moderate thermal stability ($T_{d5\%}$ = 366-385 ^oC), but relatively low glass transition temperatures (T_g = 72-142 ^oC).[23]



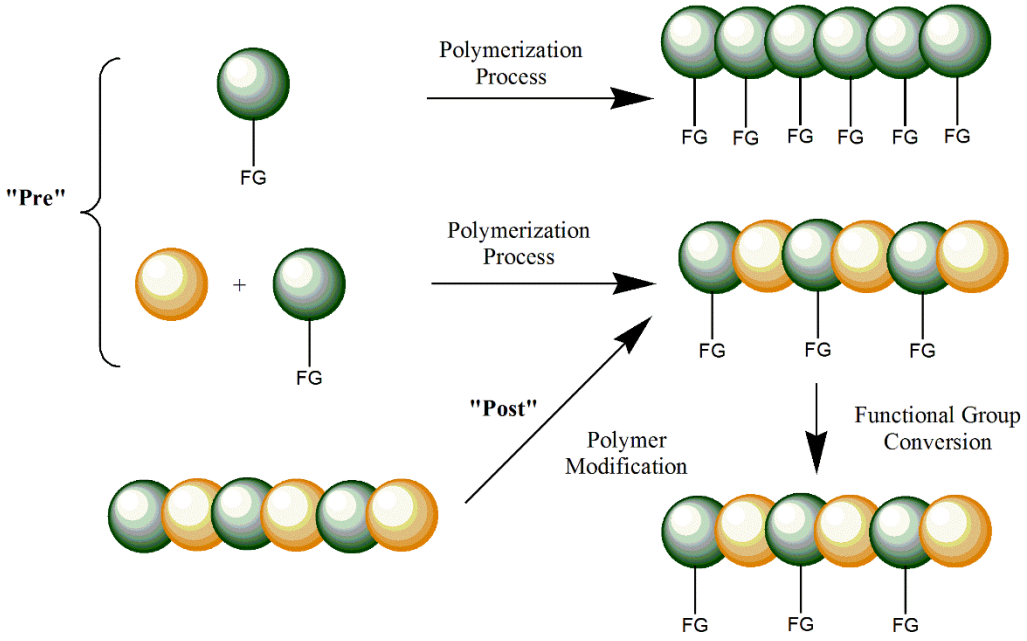
Scheme 9. NAS polycondensation activated from the *meta* positioned sulfonamide.

1.4. Introducing functionality

In order to meet a specific application need, it is a useful tool to tailor the physical and chemical properties of a polymer through introduction of functional groups to the system. This can be achieved in two ways; at the monomer stage- known as ″pre″ or ″post″- after the polymerization has been completed. The scheme for the introduction of functional groups is given in **Scheme 10**. In the ″pre″ modification, the monomer is first functionalized and then goes through the polymerization process, while in the ″post″ case the functional groups are added at the polymer stage.

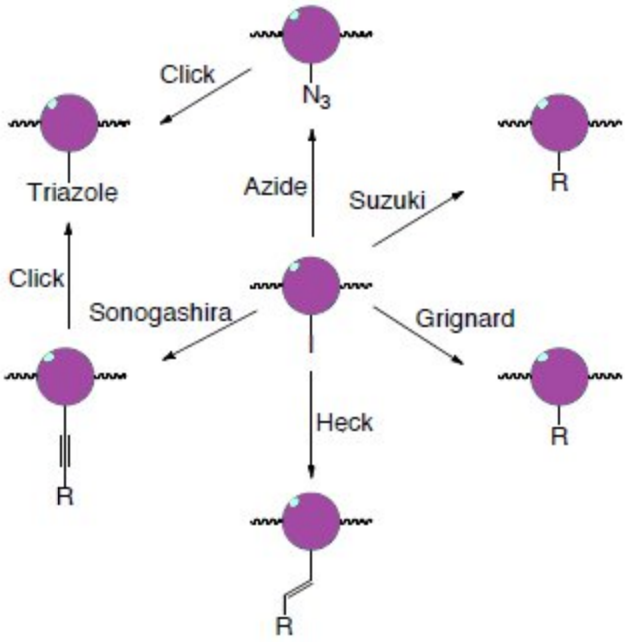
Advantages and limitations can be found in both systems. The ″pre″ modification allows control over the placement of the functional groups, however this might lead to

some undesired side reactions. In addition, the functionality within the monomer must be able to survive the polymerization conditions. On the other hand, ″post″ modification avoids side reactions that might arise in the ″pre″ case and allows the introduction of functional groups that otherwise might not have survived the polymerization conditions, nevertheless, the control over number and location of functional groups is limited.



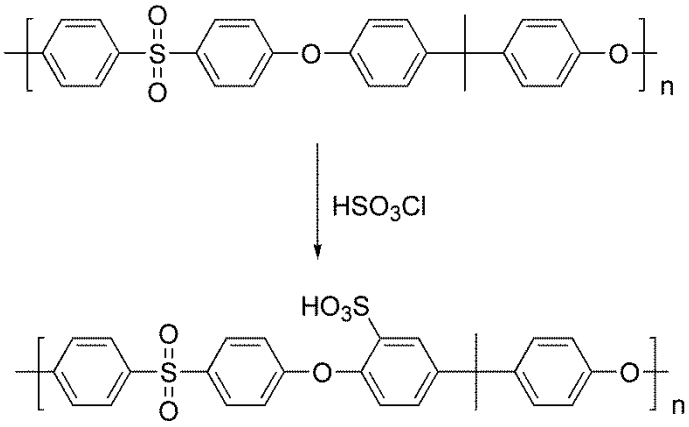
Scheme 10. Introducing functionality via pre and post modification chemistry.

In order to take advantage of both systems, an inactive functional group, such as iodides, can be introduced at the monomer level, and then converted by ″post″ modification as shown in **Scheme 11**.



Scheme 11. Post modification of aryl iodides.

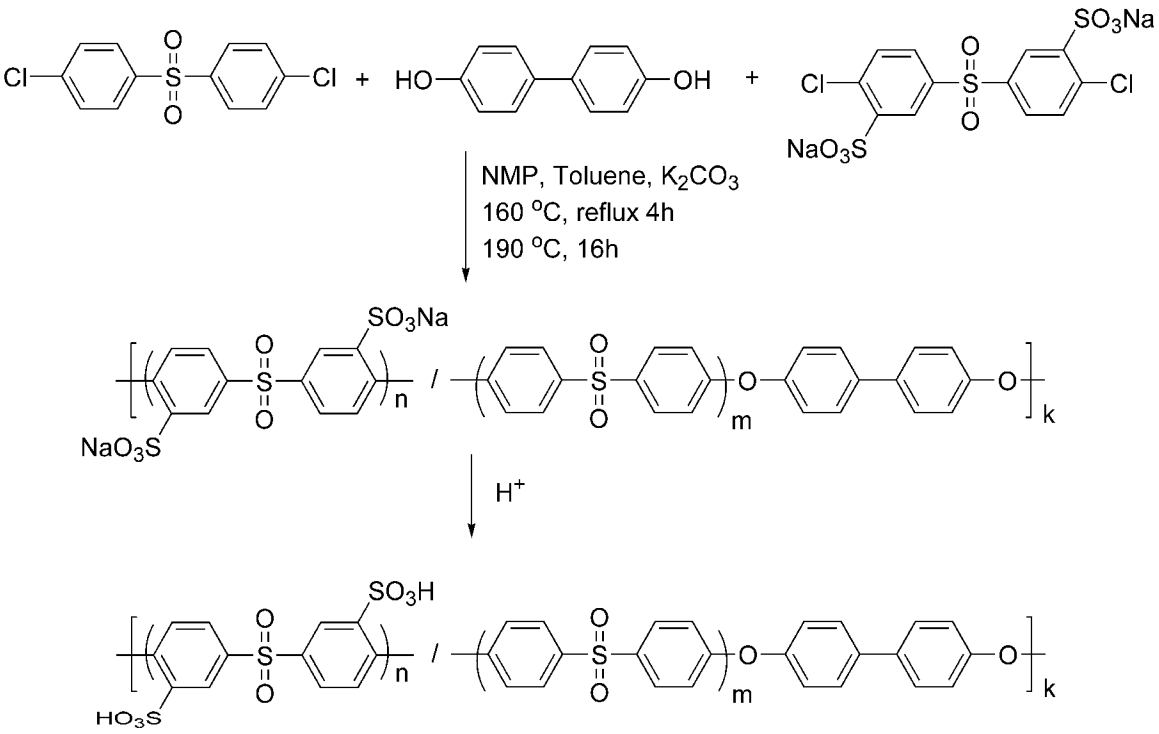
Introduction of a sulfonic acid group in poly(arylene ether sulphone)s, **PAES**, can be achieved in two ways, at the monomer stage, "pre", and after the polymerization has been completed, "post".[24] Orifice *et al* .studied the synthesis of sulfonated **PAES** via "post" modification chemistry by sulfonation with chlorosulfonic acid (**Scheme 12**),[25] however fuming sulfuric acid can also be used.[26]



Scheme 12. Synthesis of PAES via "post".

A route to the sulfonated **PAES** via "pre" modification chemistry was described by Wang *et al*. The route (**Scheme 13**) involved a reaction between the 3,3'-disulfonated-4,4'-dichlorodiphenylsulfone with the commercially available 4,4'-dichlorodiphenyl sulfone and 4,4'-biphenol.[27]

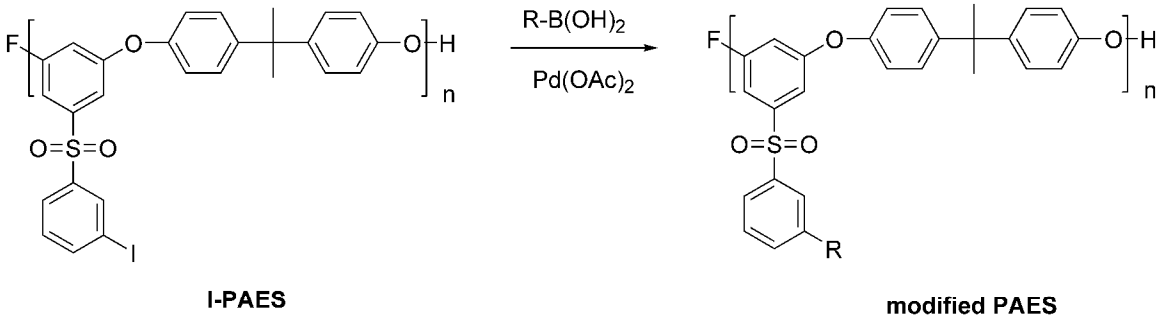
According to Wang *et al*, "pre" sulfonation of **PAES** has more advantages as the location and sulfonation level are more readily controlled, and the two sulfonic acid groups (possible only via "pre" modification) on the electron poor ring increases the stability and the acidity of the polymers.[27]



Scheme 13. Synthesis of PAES via "pre".

Our group synthesized **PAES**, with a pendant aryl iodide, via NAS polycondensation of 3-iodo-3',5'-difluoro-diphenylsulfone with Bisphenol-A. The "post" modification of the iodo polymer was achieved via Heck cross-coupling reaction using

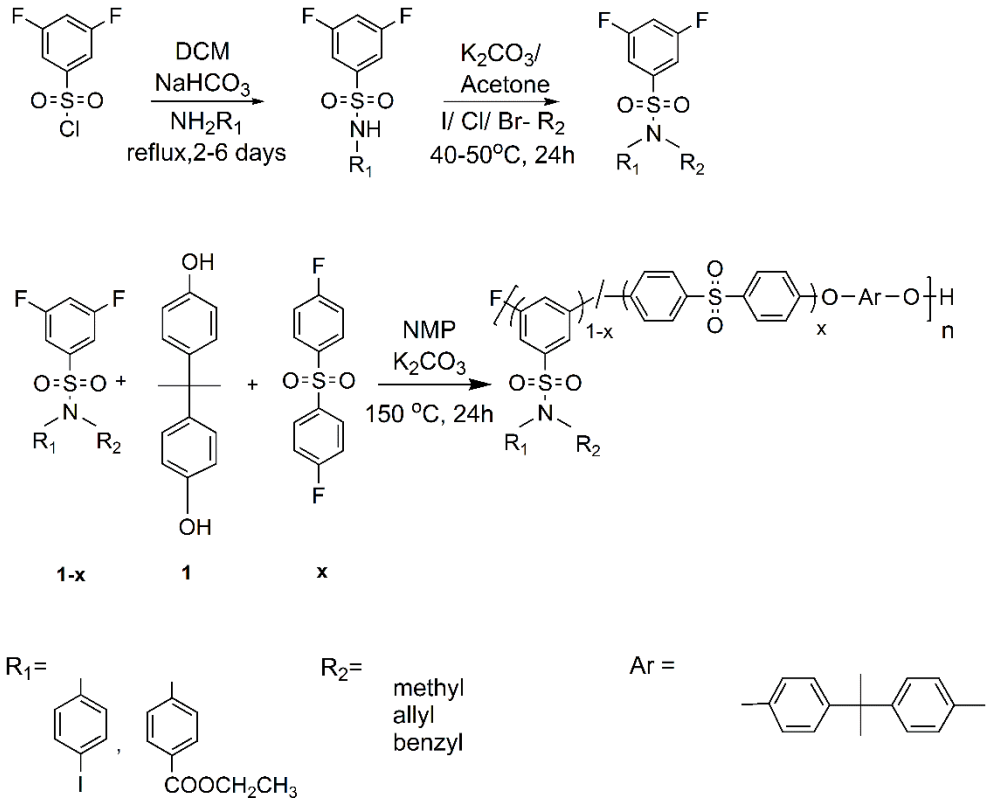
styrene and Suzuki-Miyaura cross-coupling reaction with phenyl, naphthyl, and phenylacetyl boronic acids (**Scheme 14**). The "post" modification reactions afforded a series of PAES with a variety of pendent functional groups, without any detrimental cross-linking or chain extension being observed. Since the functional groups did not reside directly on the backbone, there was little change in the thermal properties of the materials as evidenced by the narrow range of T_g values.[28]



Scheme 14. Example of post modification of aryl iodides.

1.5. Current work

In this project, the sulfonamide moiety was exploited to tailor the physical properties of PAEs by introducing a variety of functional groups, including aryl iodide, alkyl, allyl, 4-ethoxycarboxylphenyl and benzyl moieties by ″pre″ modification chemistry. A series of 3,5 difluorobenzenesulfonamide based monomers were prepared in a two-step process, followed by conversion to corresponding PAEs by reaction with Bisphenol-A, as illustrated in **Scheme 15**.



Scheme 15. Synthetic route to sulfonamide based PAEs.

2. EXPERIMENTAL

2.1. Instrumentation

^{1}H 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 an Agilent Technologies 7820A Series GC System and an Agilent Technologies 5975 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. Weight average molecular weights, M_w, and dispersity were determined using OmniSec software (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

3,5-Difluorobenzenesulfonyl chloride was purchased from Oakwood Products and used as received. 4-iodoaniline, ethyl 4-aminobenzoate, allyl bromide, iodomethane, benzyl chloride, chloroform-*d* ($CDCl_3$), and deuterated dimethylsulfoxide (DMSO-d_6), were purchased from Sigma Aldrich Chemicals Co. and used as received. ACS grade

acetone, dichloromethane (DCM), sodium bicarbonate ($NaHCO_3$) and magnesium sulfate ($MgSO_4$) were used as received from Fischer Scientific. THF was purchased from Macron and used as received. Bisphenol-A, purchased from Sigma Aldrich, was recrystallized from toluene and dried under vacuum prior to use. 4,4'-difluorodiphenyl sulfone, purchased from Sigma Aldrich, was recrystallized from ethanol and dried under vacuum prior to use. *N*-Methylpyrrolidinone, NMP (Sigma Aldrich), was dried over CaH_2 and distilled under nitrogen prior to use. Anhydrous potassium carbonate (K_2CO_3) powder (Sigma Aldrich) was dried at 130 °C in an oven before use.

2.3. Synthesis of *N*-(4-iodophenyl)-3,5-difluorobenzenesulfonamide (1)

In a 250 mL RB flask, equipped with a stir bar, reflux condenser and nitrogen gas inlet, were placed 3,5-difluorobenzenesulfonyl chloride (10.0 g, 47.2 mmol), $NaHCO_3$ (6.70 g, 80.1 mmol), 4-iodoaniline (10.3 g, 47.2 mmol), and DCM (50 mL). The flask was immersed in a mineral oil bath and heated to reflux for 48 h at which point GC/MS analysis of an aliquot confirmed conversion of starting material to the desired product. The reaction mixture was diluted with chloroform (30 mL), washed with DI water (3X 50 mL), 1M HCl (50 mL), 0.05M $NaHCO_3$ (50 mL) and finally two times with water. The organic layer was dried over $MgSO_4$, filtered and the solvents were removed by rotary evaporation to afford a light pink solid. The resulting product was recrystallized from ethanol/DI H_2O (2:1) to afford 13.9 g (74.5 %) of the desired product with a melting point of 144-146 °C. ^{1}H NMR ($CDCl_3$, δ): 6.87 (dd, 2H), 7.03 (tt, 1H), 7.33 (m, 2H), 7.60 (dd, 2H); ^{13}C NMR ($CDCl_3$, δ): 90.2 (s), 109.0 (t), 111.0 (dd), 123.6 (s), 135.2 (s), 138.6 (s), 141.8 (t), 161.1 (dd) ppm.

2.4. Synthesis of *N*-methyl-*N*-(4-iodophenyl)-3,5-difluorobenzenesulfonamide (1a)

In a 250 mL RB flask, equipped with a stir bar, reflux condenser and nitrogen gas inlet, were placed *N*-(4-iodophenyl)-3,5-difluorobenzenesulfonamide (4.00 g, 10.1 mmol), CH_3I (1.90 mL, 30.3 mmol), K_2CO_3 (2.40 g, 17.2 mmol), and acetone (30 mL). The flask was immersed in a mineral oil bath and heated to 40 ^oC for 24 h. The reaction was monitored by GC/MS, which showed completion of reaction. The reaction mixture was diluted with chloroform (20 mL) and washed with DI water (3X 50 mL), the aqueous layer was again washed with chloroform (3X 20 mL). The organic layer was dried over $MgSO_4$, filtered and the solvents were removed by rotary evaporation to afford an off white solid. The resulting product was recrystallized from ethanol/DI H_2O to afford 3.43 g (83 %) of the desired product with a melting point of 104-106 °C. ^1H NMR ($CDCl_3$, δ): 3.21 (s, 3H), 6.87 (dd, 2H), 7.06 (tt, 1H), 7.12 (m, 2H), 7.66 (dd, 2H). ^{13}C NMR ($CDCl_3$, δ): 38.1 (s), 93.0 (s), 108.6 (t), 111.4 (dd), 128.2 (s), 138.3 (s), 139.6 (s), 140.5 (t), 160.8 (dd) ppm. Elemental Analysis: Calc. Anal. for $C_{13}H_{10}F_2NO_2S$: C, 38.14; H, 2.44; Found: C, 38.33; H, 2.40.

2.5. Synthesis of *N*-allyl-*N*-(4-iodophenyl)-3,5-difluorobenzenesulfonamide (1b)

In a 100 mL RB flask, equipped with a stir bar, reflux condenser and nitrogen gas inlet, were placed *N*-(4-iodophenyl)-3,5-difluorobenzenesulfonamide (4.00 g, 10.1 mmol), allyl bromide (1.00 mL, 11.6 mmol), K_2CO_3 (2.40 g, 17.2 mmol) and acetone (35 mL). The flask was immersed in a mineral oil bath and heated to 45 ^oC for 24 h. The reaction was monitored by GC/MS, which showed completion of reaction. The reaction mixture was diluted with chloroform (20 mL) and washed with DI water (3X 50 mL) and

then the aqueous layer was washed with chloroform. The organic layers were combined, dried over $MgSO_4$, filtered and the solvents were removed by rotary evaporation to afford an off white solid. The resulting product was recrystallized from ethanol/DI H_2O to afford 3.8 g (87 %) of the desired product with a melting point of 86-88 °C. ^{1}H NMR ($CDCl_3$, δ): 4.20 (dt, 2H), 5.11 (m, 2H), 5.71 (m, 1H), 6.81 (dd, 2H), 7.06 (tt, 1H), 7.18 (m, 2H), 7.66 (dd, 2H). ^{13}C NMR ($CDCl_3$, δ): 53.8 (s), 93.9 (s), 108.4 (t), 111.2 (dd), 119.8 (s), 130.5 (s), 131.8 (s), 138.1 (s), 138.4 (s), 141.6 (t), 160.9 (dd) ppm. Elemental Analysis: Calc. Anal. for $C_{15}H_{12}F_2NO_2S$: C, 41.38; H, 2.76; Found: C, 41.44; H, 2.67.

2.6. Synthesis of *N*-benzyl-*N*-(4-iodophenyl)-3,5-difluorobenzenesulfonamide (1c)

In a 50 mL RB flask, equipped with a stir bar, reflux condenser and nitrogen gas inlet, were placed *N*-(4-iodophenyl)-3,5-difluorobenzenesulfonamide (4.00 g, 10.1 mmol), benzyl chloride (1.50 mL, 15.2 mmol), K_2CO_3 (2.40 g, 17.2 mmol) and acetone (30 mL). The flask was immersed in a mineral oil bath and heated to 50 ^{o}C for 24 h. The reaction was monitored by GC/MS, which showed completion of reaction. The reaction mixture was diluted with chloroform (20 mL) and washed with DI water (3X 50 mL) and then the aqueous layer was washed with chloroform. The organic layers were combined, dried over $MgSO_4$, filtered and the solvents were removed by rotary evaporation to afford an off white solid. The resulting product was recrystallized from methanol/DI H_2O to afford 1.85 g (38 %) of the desired product with a melting point of 142-144 °C. ^{1}H NMR ($CDCl_3$, δ): 4.73 (s, 2H), 6.73 (dd, 2H), 7.08 (tt, 1H), 7.22 (m, 7H), 7.57 (dd, 2H). ^{13}C NMR ($CDCl_3$, δ): 55.0 (s), 94.0 (s), 108.5 (t), 110.9 (dd), 128.0 (s), 128.5 (s), 128.6 (s),

130.6 (s), 134.8 (s), 137.9 (s), 138.3 (s), 141.7 (t), 161.0 (dd) ppm. Elemental Analysis: Calc. Anal. for $C_{19}H_{14}F_2NO_2S$: C, 47.01; H, 2.88; Found: C, 47.89; H, 2.77.

2.7. Synthesis of *N*-(4-ethoxycarboxylphenyl)-3,5-difluorobenzenesulfonamide (2)

In a 25 mL RB flask, equipped with a stir bar, reflux condenser and nitrogen gas inlet, were placed 3,5-difluorobenzenesulfonyl chloride (1.0 g, 4.7 mmol), $NaHCO_3$ (0.7 g, 8.1 mmol), ethyl 4-aminobenzoate (0.8 g, 4.7 mmol) and DCM (2.5 mL). The flask was immersed in a mineral oil bath and heated to 50 ^oC for 6 days. The reaction was monitored by GC/MS, which showed completion of reaction. The reaction mixture was diluted with chloroform (2 mL), washed with DI water (3X 10mL), 1M HCl (20 mL), 0.05M $NaHCO_3$ (20 mL) and finally with water (3X 20 mL). The organic layer was dried over $MgSO_4$, filtered and the solvents were removed by rotary evaporation to afford a white solid. The resulting product was recrystallized from methanol/DI H_2O to afford 1.1 g (70 %) of the desired product with a melting point of 180-182 °C. ^1H NMR (DMSO-d_6, δ): 1.26 (t, 3H), 4.23 (q, 2H), 7.26 (dd, 2H), 7.51 (tt, 1H), 7.62 (m, 2H), 7.83(dd, 2H). ^{13}C NMR (DMSO-d_6, δ): 14.5 (s), 61.0 (s), 109.6 (t), 111.2 (dd), 119.3 (s), 125.8 (s), 131.1 (s), 141.9 (s), 142.9 (t), 160.9 (dd), 165.5 (s) ppm.

2.8. Synthesis of *N*-methyl-*N*-(4-ethoxycarboxylphenyl)-3,5-difluorobenzenesulfonamide (2a)

In a 25 mL RB flask, equipped with a stir bar, reflux condenser and nitrogen gas inlet, were placed *N*-(4-ethoxycarboxylphenyl)-3,5-difluorobenzenesulfonamide (2.5 g,

7.3 mmol), iodomethane (3.00 mL, 48.0 mmol), K_2CO_3 (1.70 g, 12.5 mmol) and acetone (15 mL). The flask was immersed in a mineral oil bath and heated to 40 ^oC for 24 h. The reaction was monitored by GC/MS, which showed completion of reaction. The reaction mixture was diluted with chloroform (10 mL) and washed with DI water (3X 20 mL) and then the aqueous layer was washed with chloroform. The organic layers were combined, dried over $MgSO_4$, filtered and the solvents were removed by rotary evaporation to afford a white solid. The resulting product was recrystallized from ethanol/DI H_2O to afford 2.17 g (84 %) of the desired product with a melting point of 99-101 °C. ^1H NMR ($CDCl_3$, δ): 1.41(t, 3H), 3.26(s, 3H), 4.39(q, 2H), 7.05(tt,1H), 7.10(m, 2H), 7.22(dd, 2H), 8.02(dd, 2H). ^{13}C NMR ($CDCl_3$, δ): 14.3 (s), 38.0 (s), 61.2 (s), 108.6 (t), 110.9 (dd), 125.7 (s), 129.5 (s), 130.4 (s), 139.6 (t), 144.7 (s), 161.0 (dd), 165.6 (s) ppm. Elemental Analysis: Calc. Anal. for $C_{16}H_{15}F_2NO_4S$: C, 54.08; H, 4.22; Found: C, 54.14; H, 4.22.

2.9. Synthesis of *N*-allyl-*N*-(4-ethoxycarboxylphenyl)-3,5-difluorobenzenesulfonamide (2b)

In a 25 mL RB flask, equipped with a stir bar, reflux condenser and nitrogen gas inlet, were placed *N*-(4-ethoxycarboxylphenyl)-3,5-difluorobenzenesulfonamide (2.5 g, 7.3 mmol), allyl bromide (2.00 mL, 23.1 mmol), K_2CO_3 (1.70 g, 12.4 mmol) and acetone (15 mL). The flask was immersed in a mineral oil bath and heated to 45 ^oC for 24 h. The reaction was monitored by GC/MS, which showed completion of reaction. The reaction mixture was diluted with chloroform (10 mL) and washed with DI water (3X 20 mL) and then the aqueous layer was washed with chloroform. The organic layers were combined, dried over $MgSO_4$, filtered and the solvents were removed by rotary evaporation to afford

a white solid. The resulting product was recrystallized from methanol/DI H_2O to afford 2.41 g (86 %) of the desired product with a melting point of 111-113 °C. ^{1}H NMR ($CDCl_3$, δ): 1.40(t, 3H), 4.25(d, 2H), 4.38(q, 2H), 5.13(m, 2H), 5.72(m, 1H), 7.05(tt, 1H), 7.17(m, 4H), 8.01(dd, 2H). ^{13}C NMR ($CDCl_3$, δ): 14.3 (s), 53.6 (s), 61.2 (s), 108.5 (t), 110.8 (dd), 119.8 (s), 128.1 (s), 130.1 (s), 130.4 (s), 131.7 (s), 141.5 (t), 142.3 (s), 161.0 (dd), 165.6 (s) ppm. Elemental Analysis: Calc. Anal. for $C_{18}H_{17}F_2NO_4S$: C, 56.69; H, 4.46; Found: C, 56.74; H, 4.40.

2.10. Synthesis of *N*-benzyl-*N*-(4-ethoxycarboxylphenyl)-3,5-difluorobenzenesulfonamide (2c)

In a 25 mL RB flask, equipped with a stir bar, reflux condenser and nitrogen gas inlet, were placed *N*-(4-ethoxycarboxylphenyl)-3,5-difluorobenzenesulfonamide (2.5 g, 7.3 mmol), benzyl chloride (2.00 mL, 17.4 mmol), K_2CO_3 (1.70 g, 12.5 mmol) and acetone (15 mL). The flask was immersed in a mineral oil bath and heated to 50 ^{o}C for 48 h. The reaction was monitored by GC/MS, which showed completion of reaction. The reaction mixture was diluted with chloroform (10 mL) and washed with DI water (3X 20 mL) and then the aqueous layer was washed with chloroform. The organic layers were combined, dried over $MgSO_4$, filtered and the solvents were removed by rotary evaporator to afford a white solid. The resulting product was recrystallized from ethanol/DI H_2O to afford 2.45 g (78 %) of the desired product with a melting point of 121-122 °C. ^{1}H NMR ($CDCl_3$, δ): 1.38 (t, 3H), 4.37 (q, 2H), 4.81 (s, 2H), 7.08 (m, 3H), 7.23 (m, 7H), 7.92 (dd, 2H). ^{13}C NMR ($CDCl_3$, δ): 14.2 (s) 54.8 (s), 61.2 (s), 108.6 (t), 110.9 (dd), 128.0 (s), 128.3 (s), 128.6 (s), 130.1 (s), 130.4 (s), 134.7 (s), 141.6 (t), 142.2

(s), 161.1 (dd), 165.5 (s) ppm. Elemental Analysis: Calc. Anal. for $C_{22}H_{19}F_2NO_4S$: C, 61.25; H, 4.40; Found: C, 61.29; H, 4.36.

2.11. Polymerization of 1 a-c and 2 a-c using Bisphenol-A to form 3 a-c and 4 a-c

Polymerization of *N*-methyl-*N*-(4-iodophenyl)-3,5-difluorobenzenesulfonamide (3a)

Polymers derived from *N*-R-*N*- (4-iodophenyl)-3,5-difluorobenzenesulfonamide with different organic R groups on sulfonamide nitrogen atom and Bisphenol-A were synthesized under typical NAS conditions. As a representative example, the synthesis of the *N*-methyl-*N*-(4-iodophenyl)-3,5-difluorobenzenesulfonamide, **3a**, PAEs was as follows:

In a 10 mL RB flask equipped with a stir bar, reflux condenser and nitrogen gas inlet, were placed *N*-methyl-*N*-(4-iodophenyl)-3,5-difluorobenzenesulfonamide (1.00 g; 2.45 mmol), Bisphenol-A (557 mg; 2.45 mmol), K_2CO_3 (1.01 g; 3.00 mmol) and NMP (3.82 mL). The flask was immersed in a silicone oil bath, stirred and heated to 150 ^oC for a period of 24 h at which point it was cooled to room temperature, diluted with NMP (3 mL) and precipitated from 1000 mL of vigorously stirred, slightly acidic (pH~5) water. The resulting precipitate isolated via filtration was stirred in DI water and filtered. The solids were dissolved in THF and reprecipitated from ethanol, filtered and dried under vacuum to afford (1.2 g, 82%) of a white solid. ^1H NMR ($CDCl_3$, δ): 1.73 (s, 6H), 3.13 (s, 3H), 6.77 (dd, 2H), 6.87 (m, 7H), 7.28 (m, 4H), 7.55 (dd, 2H). ^{13}C NMR ($CDCl_3$, δ): 25.6, 38.0, 42.5, 68.0, 92.4, 110.5, 112.2, 116.7, 119.2, 128.1, 128.5, 138.0, 141.1, 147.0, 153.0, 159.3 ppm.

(3b) (52 %). ^{1}H NMR ($CDCl_3$, δ): 1.73 (s, 6H), 4.12 (dt, 2H), 5.07 (m, 2H), 5.66 (m, 1H), 6.87 (m, 9H), 7.23 (m, 4H), 7.58 (dd, 2H). ^{13}C NMR ($CDCl_3$, δ): 31.1, 42.4, 53.5, 93.3, 110.6, 112.3, 119.1, 119.4, 128.5, 130.4, 132.2, 138.1, 138.6, 140.1, 147.0, 159.4, 153.1 ppm.

(3c) (68 %) ^{1}H NMR ($CDCl_3$, δ): 1.73 (s, 6), 4.68 (s, 2H), 6.72 (dd, 2H), 6.91 (m, 6H), 7.21 (m, 8H), 7.49 (dd, 2H). ^{13}C NMR ($CDCl_3$, δ): 31.0, 42.4, 54.6, 93.4, 110.6, 112.3, 119.1, 127.8, 128.4, 128.4, 128.5, 130.5, 135.2, 138.1, 138.4, 140.3, 146.9, 153.1, 159.4 ppm.

Polymerization of *N*-methyl-*N*-(4-ethoxycarboxylphenyl)-3,5-difluorobenzenesulfonamide (4a)

Polymers derived from *N*-R-*N*-(4-ethoxycarboxylphenyl)-3,5-difluorobenzenesulfonamide with different organic R groups on sulfonamide nitrogen atom and Bisphenol-A were synthesized under typical NAS conditions. As a representative example, the synthesis of the *N*-methyl-*N*-(4-ethoxycarboxylphenyl)-3,5-difluorobenzenesulfonamide, **4a**, PAEs was as follows:

In a 10 mL RB flask, equipped with a stir bar, reflux condenser and nitrogen gas inlet, were placed *N*-methyl-*N*-(4-ethoxycarboxylphenyl)-3,5-difluorobenzenesulfonamide (887.5 mg; 2.500 mmol), Bisphenol-A (570 mg; 2.50 mmol), K_2CO_3 (1036.5 mg; 3.0000 mmol) and NMP (3.90 mL). The flask was immersed in a silicone oil bath, stirred and heated to 150 ^{o}C for a period of 24 h, at which point it was cooled to room temperature, diluted with THF (5 mL) and precipitated from 3000

mL of vigorously stirred, slightly acidic (pH~5) water. The resulting precipitate isolated via filtration was stirred in DI water and filtered. The solids were dissolved in THF and reprecipitated from isopropanol, filtered and dried under vacuum to afford (0.44 g, 32 %) of white solids. ^{1}H NMR ($CDCl_3$, δ): 1.37 (t, 3H), 1.68 (s, 6H), 3.19 (s, 3H), 4.35 (q, 2H), 6.83 (m, 7H), 7.18 (m, 6H), 7.96 (dd, 2). ^{13}C NMR ($CDCl_3$, δ): 14.3 , 30.9, 37.9, 42.3, 61.2, 110.5, 112.2, 119.2, 125.4, 128.4, 128.8, 130.3, 138.2, 145.3, 146.9, 153.0, 159.4, 165.7 ppm.

(4b) (16%) ^{1}H NMR ($CDCl_3$, δ): 1.37 (t, 3H), 1.68 (s, 6H), 4.35 (m, 4H), 5.05 (m, 2H), 5.69 (m, 1H), 6.86 (m, 8H), 7.17 (m, 7H), 7.99 (dd, 2H). ^{13}C NMR($CDCl_3$, δ): 14.3, 30.8, 42.3, 53.2, 61.2, 110.5, 112.2, 119.1, 119.4, 127.9, 128.3, 129.4, 130.2, 132.1, 140.1, 142.9, 146.8, 153.1, 159.4, 165.6 ppm.

(4c) (36%) ^{1}H NMR ($CDCl_3$, δ): 1.31 (t, 3H), 1.67 (s, 6H), 4.30 (q, 2H), 7.17 (m, 16 H), 7.88 (dd, 2H). ^{13}C NMR ($CDCl_3$, δ): 14.2, 30.8, 42.3, 54.4, 61.1, 110.5, 112.2, 119.1, 127.8, 128.1, 128.3, 128.3, 128.5, 129.5, 130.2, 135.1, 140.3, 142.7, 146.9, 153.1, 159.5, 165.6 ppm.

2.12. Random copolymer synthesis

Random copolymers with different organic groups on the sulfonamide nitrogen atom were synthesized under typical NAS polymerization conditions of varying ratios of *N*-R-*N*-(ethoxycarboxylphenyl)-3,5-difluorobenzenesulfonamide, *N*-R-*N*-(4-iodophenyl)-3,5-difluorobenzenesulfonamide and 4,4'-difluorodiphenyl sulfone with Bisphenol-A. A

copolymer, **5a**, with 25% *N*-methyl-*N*-(4-iodophenyl)-3,5-difluorobenzenesulfonamide (**1a**) monomer, was synthesized as follows:

In a 10 mL RB flask, equipped with a stir bar, reflux condenser and nitrogen gas inlet, were placed *N*-methyl-*N*-(4-iodophenyl)-3,5-difluorobenzenesulfonamide (255.6 mg; 0.625 mmol), Bisphenol-A (570 mg; 2.50 mmol), 4,4'-difluorodiphenyl sulfone (476.2 mg, 1.875 mmol), K_2CO_3 (1036.5 mg; 3.0000 mmol) and NMP (3.90 mL). The flask was immersed in a silicone oil bath, stirred and heated to 150 ^oC for a period of 24 h, at which point it was cooled to room temperature, diluted with THF (5 mL) and precipitated from 3000 mL of vigorously stirred, slightly acidic (pH~5) water. The resulting precipitate isolated via filtration was stirred in water and filtered. The solids were dissolved in THF and reprecipitated from isopropanol, filtered and dried under vacuum to afford (0.84 g, 71 %) of white solids.

NMR peaks for 10% copolymers had the same chemical shifts as the one reported above with varying intensities depending on the ratio of the monomer used.

All polymers with varying monomer ratios (25% and 10%) were synthesized following the same procedure with the same reaction conditions. The following yields were obtained: **5b** 79%, **6a** 77%, **6b** 64%, **7a** 77%, **7b** 88%, **8a** 77%, **8b** 77%, **9a** 56%, **9b** 65%, **10a** 50%, **10b** 64%.

2.13. Characterization

2.13.1. Thermogravimetric Anaysis (TGA)

The thermal stability of the polymers was investigated using a TA Instruments Q500 Thermogravimetric Analyzer. The analysis involved heating a 5 mg of sample, at a rate of 10 °C/min., from 40 ° C to 800 °C under nitrogen or air atmosphere. The weight loss was recorded as a function of temperature and the thermal stability was reported as 5 % weight loss.

2.13.2. 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 T_{zero} aluminum pan, at 10 ºC/min from 40 ºC to 215 ºC and cooling at 10 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.

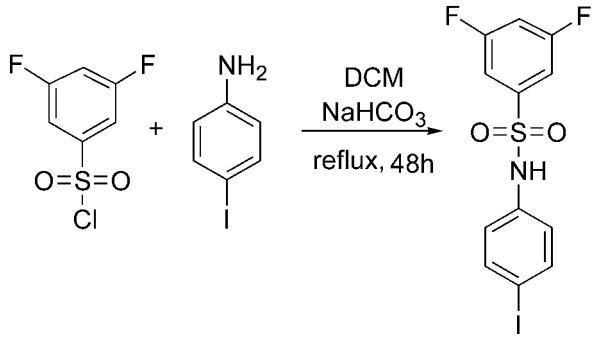
2.13.3. Size Exclusion Chromatography (SEC)

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 the light scattering signal. Calibration was done using polystyrene standards.

3. RESULTS AND DISCUSSION

3.1. Synthesis of *N*-(4-iodophenyl)-3,5-difluorobenzenesulfonamide (1)

A series of functionalized poly(arylene ether)s, PAEs, based on 3,5-difluorobenzene sulfonamides with varying groups present on the sulfonamide moiety were investigated. Using 3,5-difluorobenzenesulfonyl chloride as a starting material, *N*-(4-iodophenyl)-3,5-difluorobenzenesulfonamide **(1)** was prepared via nucleophilic substitution, as shown in **Scheme 16.** Commercially available 3,5-difluorobenzenesulfonyl chloride was allowed to react with 4-iodoaniline in DCM and heated to reflux for 48h, at which point analysis by GC/MS confirmed conversion of the starting materials to the desired product. The product was recrystallized from ethanol/DI H_2O to afford 75 % yield.



Scheme 16. Synthesis of *N*-(4-iodophenyl)-3,5-difluorobenzenesulfonamide **(1)**.

The structure was confirmed by ^{1}H and ^{13}C NMR spectroscopy, GC/MS and elemental analysis. The ^{1}H and ^{13}C NMR spectra of **1** are presented in **Figure 4** and **Figure 5**, respectively. There are four unique peaks that appear in the ^{1}H NMR spectrum of **1** (**Figure 4**). The most upfield proton, **c**, at 6.87 ppm gives rise to a doublet. Proton **a**, at 7.03 ppm, appears as a triplet of triplets due to coupling with two fluorines with

equivalent coupling constants ($^3J_{H\text{-}F}$ = 8.40 Hz) and two protons with equivalent coupling constants ($^4J_{H\text{-}H}$ = 2.31 Hz). Proton **b**, at 7.33 ppm, appears as a complex multiplet and proton **d**, at 7.60 ppm, was identified as a doublet.

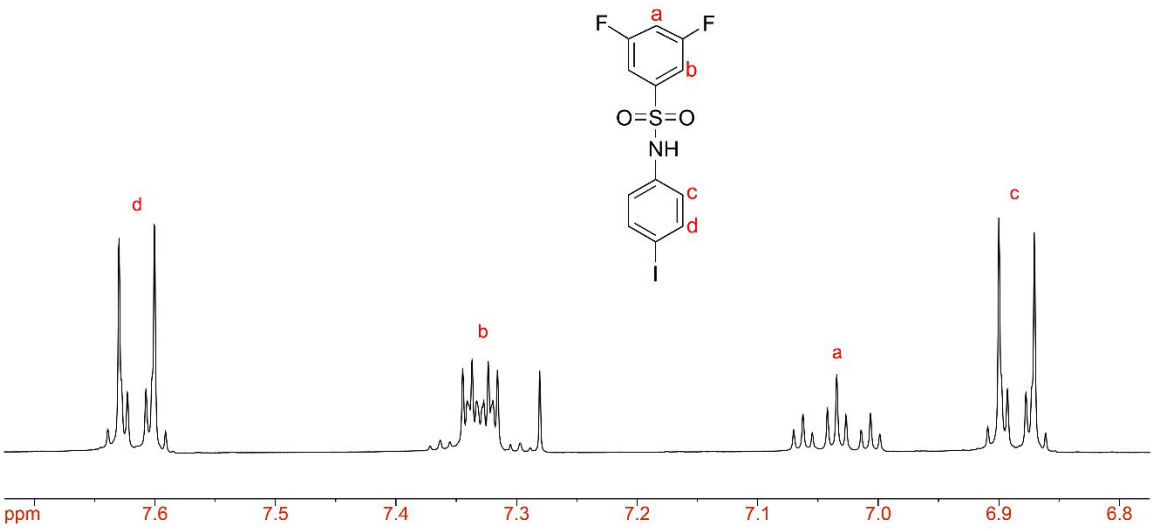


Figure 4. 300 MHz ^{1}H NMR spectrum ($CDCl_3$) of **1**.

The ^{13}C NMR spectrum (**Figure 5**) contains eight unique signals. It can be seen that there is some splitting of several signals, due to coupling with the fluorine atoms. Carbon **a** at 109.0 ppm appears as a triplet due to coupling with two equivalent *ortho* fluorines ($^2J_{C\text{-}F}$ = 25.0 Hz). Carbon **c** at 111.0 ppm gives rise to a doublet of doublets due to coupling with one *ortho* fluorine ($^2J_{C\text{-}F}$ = 28.1 Hz) and a *para* fluorine ($^4J_{C\text{-}F}$ = 8.87 Hz). Due to electron donation by the fluorine atoms in the *ortho* or *para* position, the signals for carbons **a** and **c** are shifted upfield. Carbon **d** at 141.8 ppm was identified as a triplet due to coupling with two *meta* fluorines with equivalent coupling constants ($^3J_{C\text{-}F}$ = 8.56 Hz). Carbon **b** at 161.1 ppm appears as a doublet of doublets due to coupling with

the fluorine on the *ipso* carbon ($^1J_{C\text{-}F}$ = 243.8 Hz) and a *meta* fluorine ($^3J_{C\text{-}F}$ = 11.6 Hz). All of the remaining peaks in the spectrum appear as singlets.

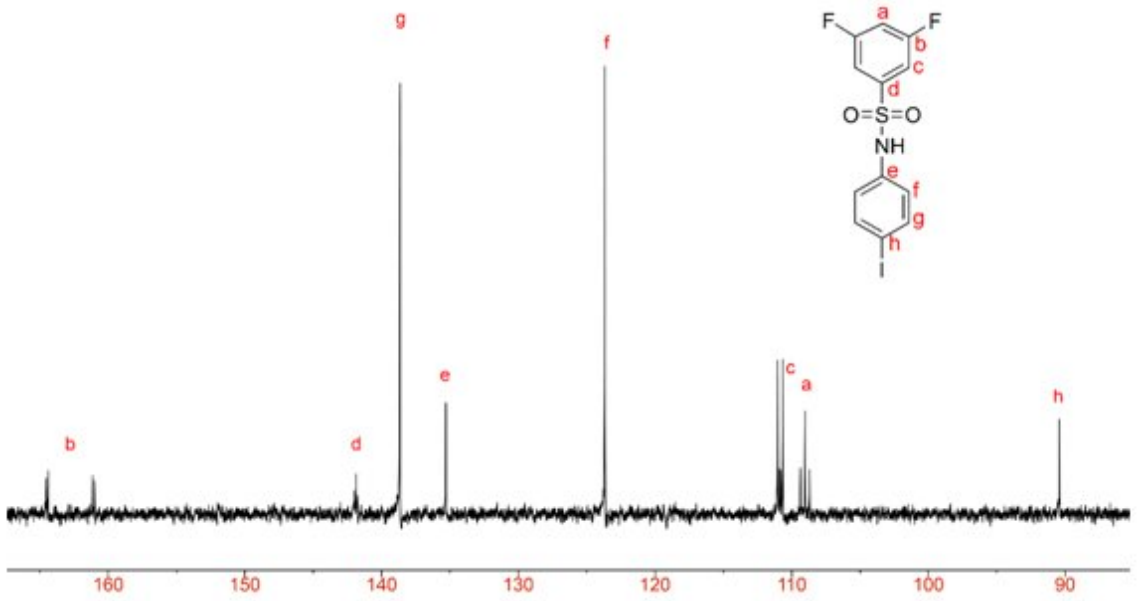
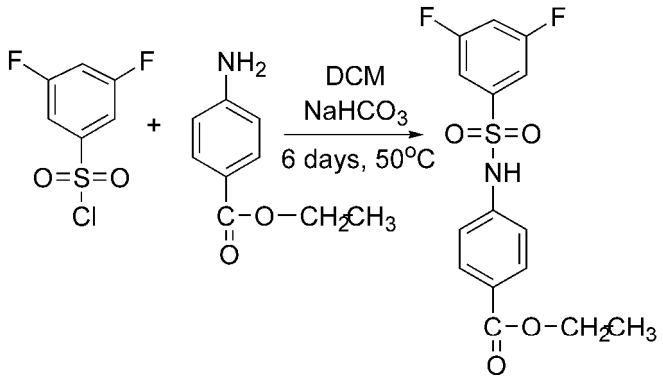


Figure 5. 75.5 MHz ^{13}C NMR spectrum ($CDCl_3$) of **1**.

3.2. Synthesis of *N*-(4-ethoxycarboxylphenyl)-3,5-difluorobenzenesulfonamide (2)

Using 3,5-difluorobenzenesulfonyl chloride as a starting material, *N*-(4-ethoxycarboxylphenyl)-3,5-difluorobenzenesulfonamide **(2)** was prepared via nucleophilic substitution, as shown in **Scheme 17**. Commercially available 3,5-difluorobenzenesulfonyl chloride was allowed to react with ethyl 4-aminobenzoate in DCM for 6 days. The reaction mixture was heated to 50 ^oC, at which point analysis by GC/MS confirmed conversion of the starting materials to the desired product. The product was recrystallized from methanol/DI H_2O to afford 70 % yield.



Scheme 17. Synthesis of *N*-(4-ethoxycarboxylphenyl)-3,5-difluorobenzenesulfonamide **(2)**.

The structure was confirmed by ^{1}H and ^{13}C NMR spectroscopy, GC/MS and elemental analysis. The ^{1}H and ^{13}C NMR spectra of **2** are presented in **Figure 6** and **Figure 7**, respectively. There are six unique peaks that appear in the ^{1}H NMR spectrum of **2** (**Figure 6**). The most upfield proton, **f**, at 1.26 ppm appears as triplet, proton **e** at 4.23 ppm gives rise to a quartet, the ethyl group in the alkyl region, proton **c** at 7.26 ppm appears as a doublet. Proton **a**, at 7.51 ppm, was identified as a triplet of triplets due to coupling with two fluorines with equivalent coupling constants ($^{3}J_{H\text{-}F}$ = 9.14 Hz) and two protons with equivalent coupling constants ($^{4}J_{H\text{-}H}$ = 2.32 Hz). Proton **b**, at 7.62 ppm, gave rise to a complex multiplet and proton **d**, at 7.83 ppm, appears as a doublet.

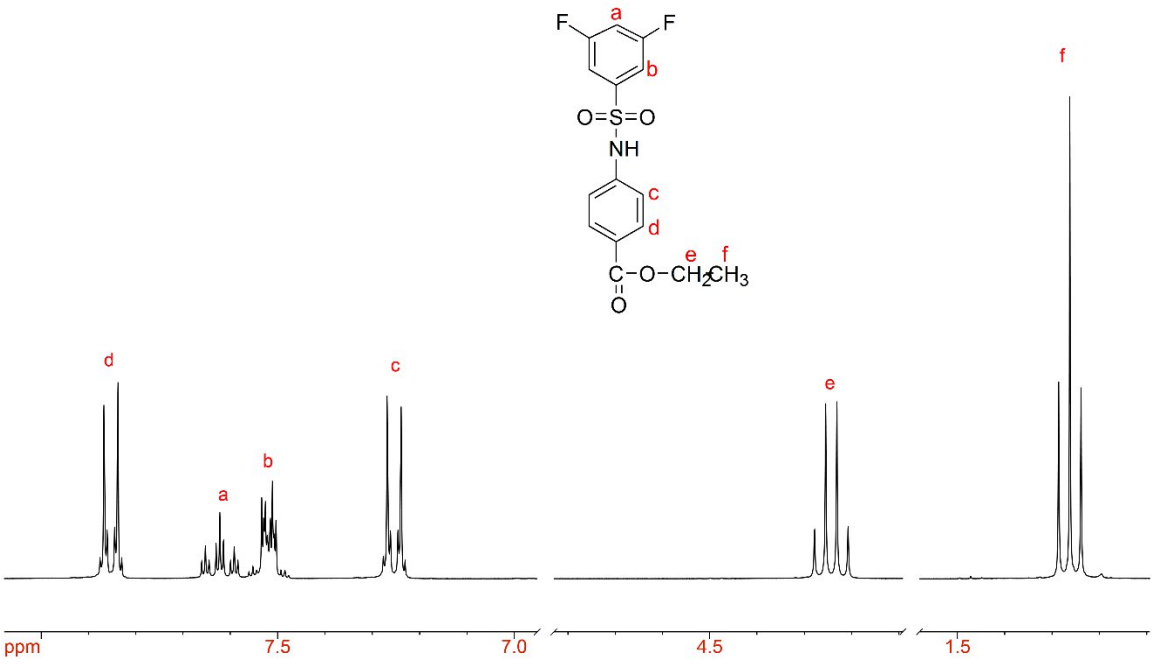


Figure 6. 300 MHz ^{1}H NMR spectrum (DMSO-d_6) of **2**.

The ^{13}C NMR spectrum (**Figure 7**) contains eleven unique signals. It can be seen that there is some splitting of several signals, due to coupling with the fluorine atoms. Carbon **a**, at 109.6 ppm, appears as a triplet due to coupling with two equivalent *ortho* fluorines ($^{2}J_{C\text{-}F}$ = 25.7 Hz). Carbon **c** at 111.2 ppm gives rise to a doublet of doublets due to coupling with one *ortho* fluorine ($^{2}J_{C\text{-}F}$ = 28.2 Hz) and a *para* fluorine ($^{4}J_{C\text{-}F}$ = 8.80 Hz). Due to electron donation by the fluorine atoms in the *ortho* or *para* position, the signals for carbons **a** and **c** are shifted upfield. Carbon **d** at 142.9 ppm appears as a triplet due to coupling with two *meta* fluorines with equivalent coupling constants ($^{3}J_{C\text{-}F}$ = 8.56 Hz). Carbon **b** at 160.9 ppm was identified as a doublet of doublets due to coupling with the fluorine on the *ipso* carbon ($^{1}J_{C\text{-}F}$ = 252.2 Hz) and a *meta* fluorine ($^{3}J_{C\text{-}F}$ = 12.4 Hz). All of the remaining peaks in the spectrum appear as singlets.

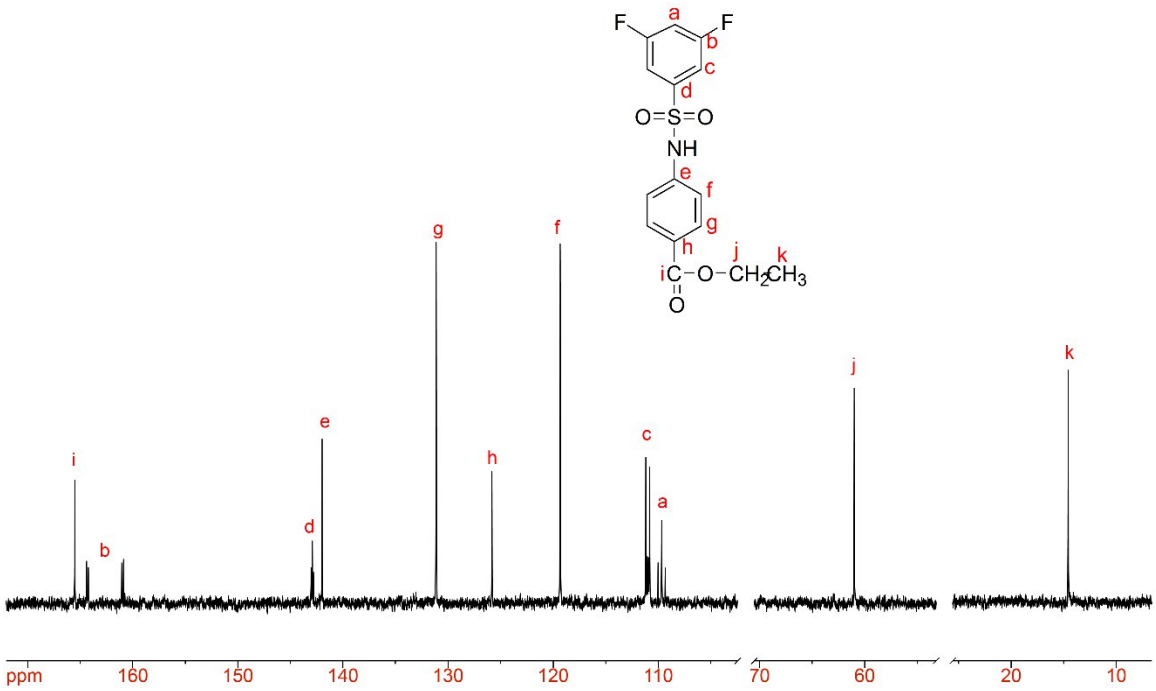


Figure 7. 75.5 MHz ^{13}C NMR spectrum (DMSO-d_6) of **2**.

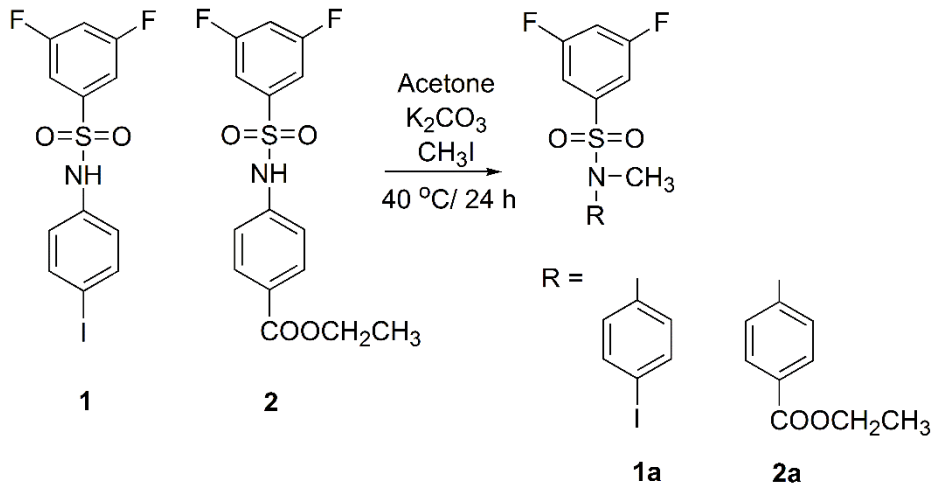
3.3. Monomer synthesis (1 a-c, 2 a-c)

Synthesis of *N*-methyl-*N*-(4-iodophenyl)-3,5-difluorobenzenesulfonamide (1a)

Synthesis of *N*-methyl-*N*-(4-ethoxycarboxylphenyl)-3,5-difluorobenzenesulfonamide (2a)

The synthesis of *N*-methyl-*N*-(4-iodophenyl)-3,5-difluorobenzenesulfonamide (**1a**) and *N*-methyl-*N*-(4-ethoxycarboxylphenyl)-3,5-difluorobenzenesulfonamide (**2a**), respectively was achieved by methylation of **1** and **2**, with iodomethane as shown in **Scheme 18**. In order to deprotonate the monomer **1** and **2,** potassium carbonate was used for creating a nucleophile for the S_N2 reactions with iodomethane. The reaction mixtures were heated to 40 °C for 24 h at which point analysis by GC/MS confirmed conversion of the starting materials to the desired products. The product was obtained after work-up which involved diluting the reaction mixtures with chloroform, extraction with water,

evaporation to dryness, followed by recrystallization from ethanol/water. Both structures were confirmed by ^{1}H and ^{13}C NMR spectroscopy, GC/MS and elemental analysis.



Scheme 18. Synthesis of methylated 3,5-difluorobenzene sulfonamides (**1a**) and (**2a**).

The ^{1}H and ^{13}C NMR spectra of compound **1a** are illustrated in **Figure 8** and **Figure 9,** respectively. There are five unique peaks that appear in the ^{1}H NMR spectrum of **1a** (**Figure 8**). The most upfield proton **e** at 3.21 ppm appears as a singlet, proton **c** and proton **d**, at 6.87 and 7.66 ppm, respectively appear as doublets. Proton **a**, at 7.06 ppm, was identified as a triplet of triplets due to coupling with two fluorines with equivalent coupling constants ($^{3}J_{H\text{-}F}$ = 8.40 Hz) and two protons with equivalent coupling constants ($^{4}J_{H\text{-}H}$ = 2.31 Hz). Proton **b**, at 7.12 ppm, appears as a complex multiplet and partially overlaps with proton **a**.

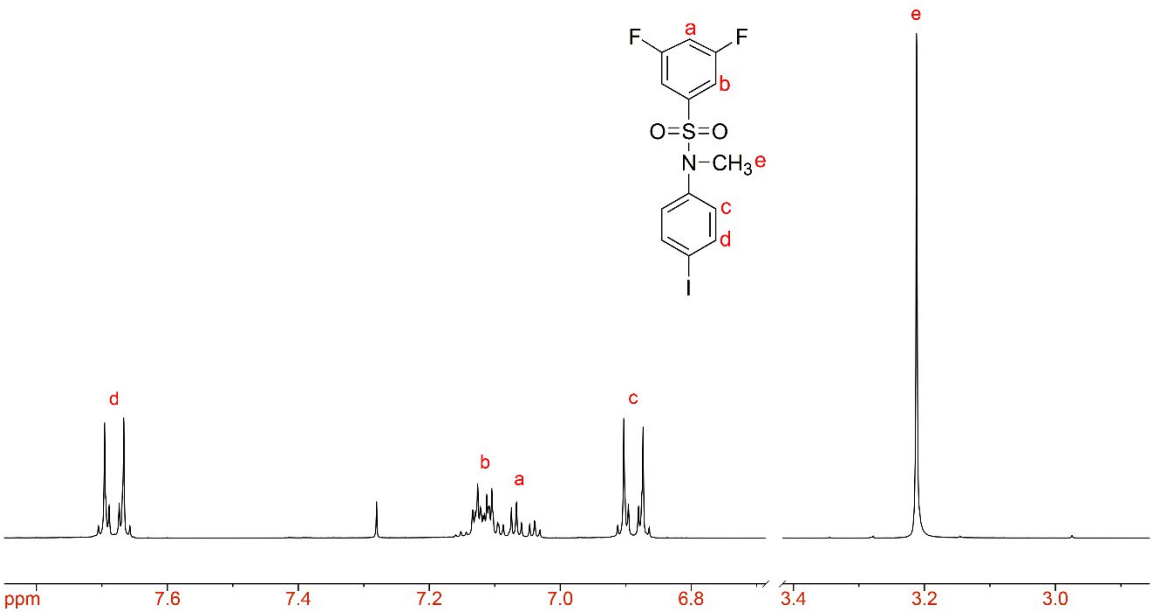


Figure 8. 300 MHz ^{1}H NMR spectrum ($CDCl_3$) of **1a**.

The ^{13}C NMR spectrum (**Figure 9**) contains nine unique signals. It can be seen that there is some splitting of several signals, due to coupling with the fluorine atoms. Carbon **a** at 108.6 ppm appears as a triplet due to coupling with two equivalent *ortho* fluorines ($^{2}J_{C\text{-}F}$ = 24.99 Hz). Carbon **c** at 111.4 ppm gives rise to a doublet of doublets due to coupling with one *ortho* fluorine ($^{2}J_{C\text{-}F}$ = 28.10 Hz) and a *para* fluorine ($^{4}J_{C\text{-}F}$ = 8.87 Hz). Due to electron donation by the fluorine atoms in the *ortho* or *para* position, the signals for carbons **a** and **c** are shifted upfield. Carbon **d** at 140.5 ppm was identified as a triplet due to coupling with two *meta* fluorines with equivalent coupling constants ($^{3}J_{C\text{-}F}$ = 8.56 Hz). Carbon **b** at 160.8 ppm appears as a doublet of doublets due to coupling with the fluorine on the *ipso* carbon ($^{1}J_{C\text{-}F}$ = 243.8 Hz) and a *meta* fluorine ($^{3}J_{C\text{-}F}$ = 11.6 Hz). All of the remaining peaks in the spectrum appear as singlets.

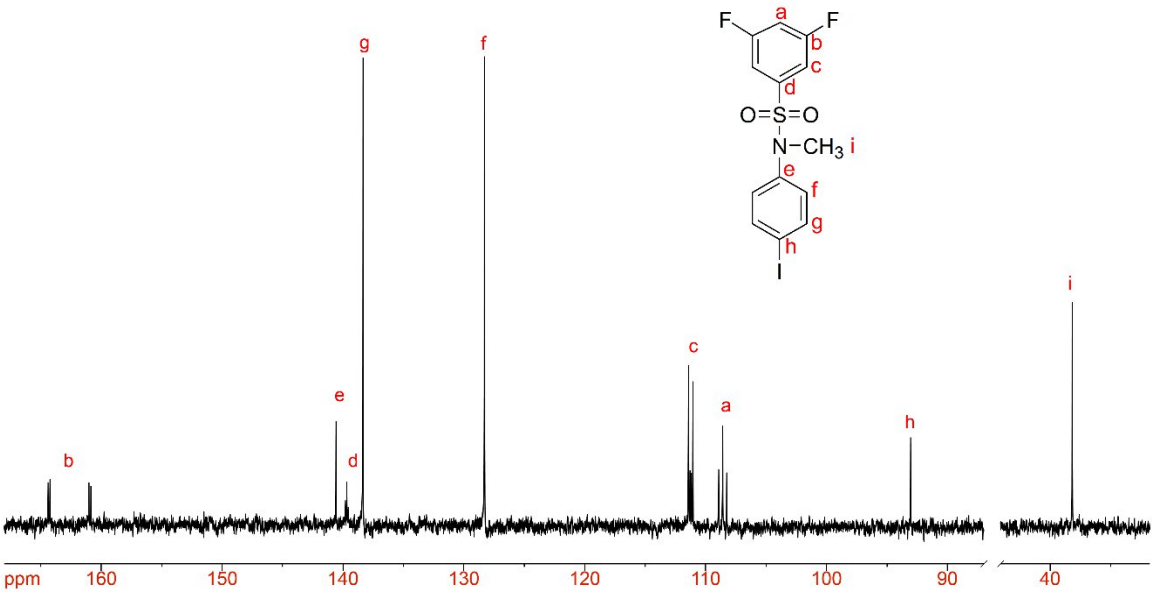


Figure 9. 75.5 MHz ^{13}C NMR spectrum ($CDCl_3$) of **1a**.

The ^{1}H and ^{13}C NMR spectra of compound **2a** are presented in **Figure 10** and **Figure 11**, respectively. There are six unique peaks that appear in the ^{1}H NMR spectrum of **2a** (**Figure 10**). The most upfield proton, **f**, at 1.41 ppm appears as a triplet, proton **g** at 3.26 ppm gives rise to a singlet, proton **e** at 4.39 ppm was identified as quartet, all in the alkyl region. Proton **c** and proton **d** at 7.22 and 8.02 ppm, respectively, appear as doublets. Proton **a**, at 7.05 ppm, appears as a triplet of triplets due to coupling with two fluorines with equivalent coupling constants ($^{3}J_{H\text{-}F}$ = 9.14 Hz) and two protons with equivalent coupling constants ($^{4}J_{H\text{-}H}$ = 2.32 Hz). Proton **b**, at 7.10 ppm, gives rise to a complex multiplet and partially overlaps with proton **a**.

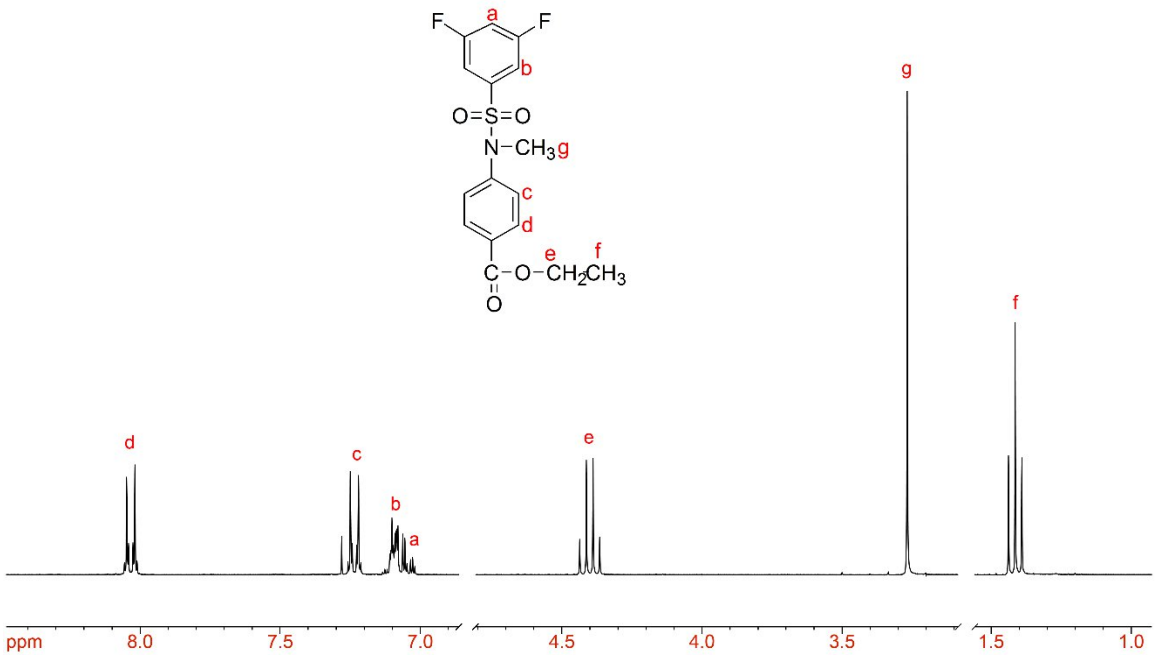


Figure 10. 300 MHz ^{1}H NMR spectrum ($CDCl_3$) of **2a**.

The ^{13}C NMR spectrum (**Figure 11**) contains eleven unique signals. It can be seen that there is some splitting of several signals, due to coupling with the fluorine atoms. Carbon **a**, at 108.6 ppm, appears as a triplet due to coupling with two equivalent *ortho* fluorines ($^{2}J_{C\text{-}F}$ = 25.73 Hz). Carbon **c** at 110.9 ppm gives rise to a doublet of doublets due to coupling with one *ortho* fluorine ($^{2}J_{C\text{-}F}$ = 28.17 Hz) and a *para* fluorine ($^{4}J_{C\text{-}F}$ = 8.80 Hz). Due to electron donation by the fluorine atoms in the *ortho* or *para* position, the signals for carbons **a** and **c** are shifted upfield. Carbon **d** at 139.6 ppm was identified as a triplet due to coupling with two *meta* fluorines with equivalent coupling constants ($^{3}J_{C\text{-}F}$ = 8.56 Hz). Carbon **b** at 161.0 ppm appears as a doublet of doublets due to coupling with the fluorine on the *ipso* carbon ($^{1}J_{C\text{-}F}$ = 252.2 Hz) and a *meta* fluorine ($^{3}J_{C\text{-}F}$ = 12.4 Hz). All of the remaining peaks in the spectrum appear as singlets.

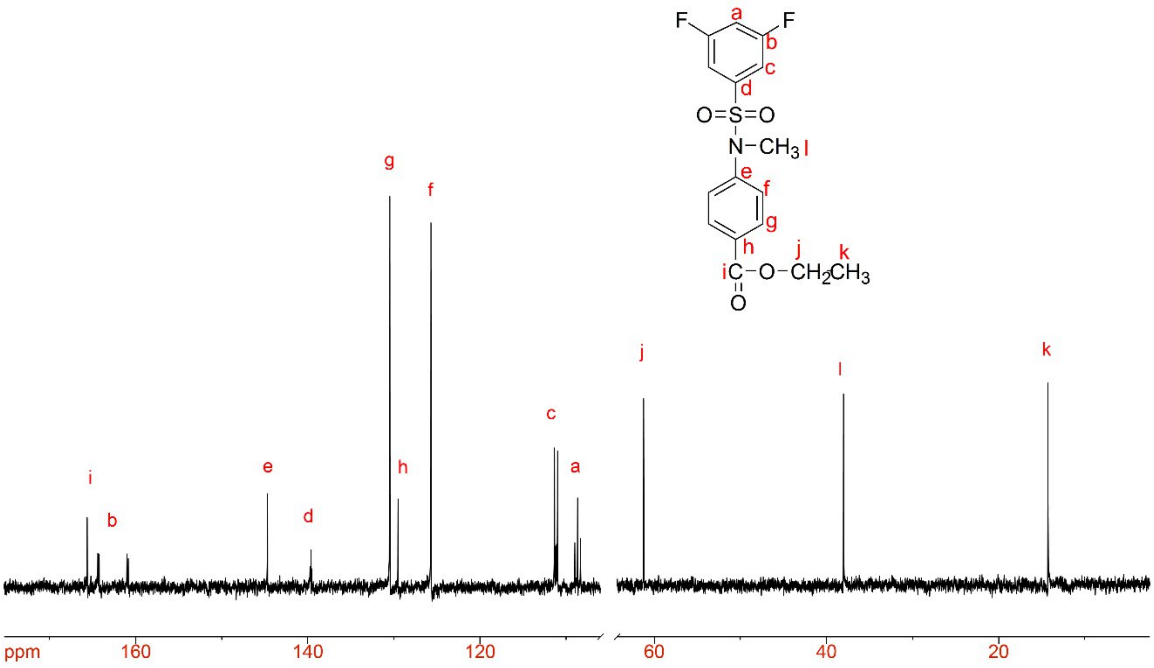


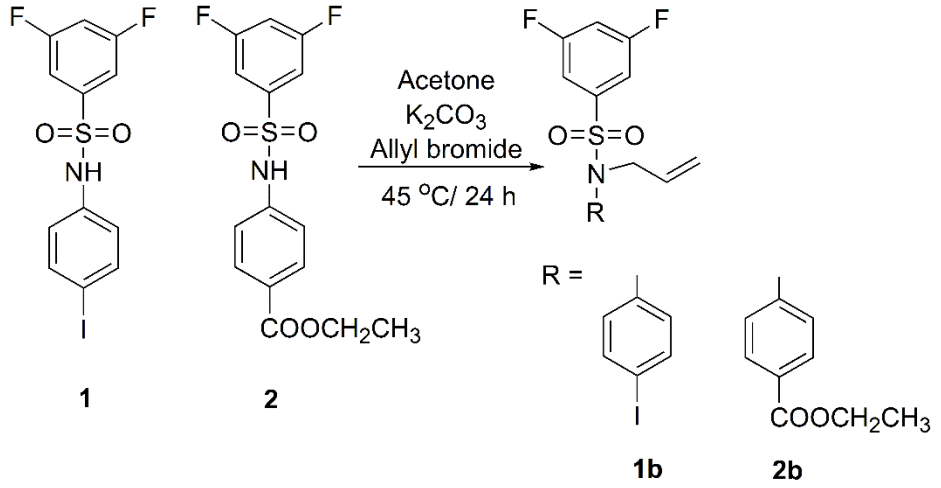
Figure 11. 75.5 MHz ^{13}C NMR spectrum ($CDCl_3$) of **2a**.

Synthesis of *N*-allyl-*N*-(4-iodophenyl)-3,5-difluorobenzenesulfonamide (1b)

Synthesis of *N*-allyl-*N*-(4-ethoxycarboxylphenyl)-3,5-difluorobenzenesulfonamide (2b)

The synthesis of *N*-allyl-*N*-(4-iodophenyl)-3,5-difluorobenzenesulfonamide (**1b**) and *N*-allyl-*N*-(4-ethoxycarboxylphenyl)-3,5-difluorobenzenesulfonamide (**2b**), respectively was achieved by allylation of **1** and **2**, with allyl bromide as shown in **Scheme 19** . In order to deprotonate the monomer **1** and **2,** potassium carbonate was used to form the nucleophile for S_N2 reactions with allyl bromide. The reaction mixtures were heated to 45 °C for 24 h at which point analysis by GC/MS confirmed conversion of the starting materials to the desired product. The product was obtained after work-up which involved diluting the reaction mixtures with chloroform, extraction with water,

evaporation to dryness, followed by recrystallization from ethanol/water for **1b** and recrystallization from methanol/water for **2b.** Both structures were confirmed by ^{1}H and ^{13}C NMR spectroscopy, GC/MS and elemental analysis.



Scheme 19. Synthesis of allylated 3,5-difluorobenzene sulfonamides (**1b)** and (**2b)**.

The ^{1}H and ^{13}C NMR spectra of compound **1b** are shown in **Figure 12** and **Figure 13,** respectively. There are seven unique peaks that appear in the ^{1}H NMR spectrum of **1b** (**Figure 12**). The most upfield proton **e** at 4.20 ppm gives rise to a doublet of triplets, protons **g** and **f** appear as complex multiplets at 5.11 and 5.71 ppm, respectively. Proton **c** and proton **d**, at 6.81 and 7.66 ppm, respectively were identified as doublets. Proton **a**, at 7.06 ppm, appears as a triplet of triplets due to coupling with two fluorines with equivalent coupling constants ($^{3}J_{H\text{-}F}$ = 8.40 Hz) and two protons with equivalent coupling constants ($^{4}J_{H\text{-}H}$ = 2.31 Hz). Proton **b**, at 7.18 ppm, gives rise to a complex multiplet.

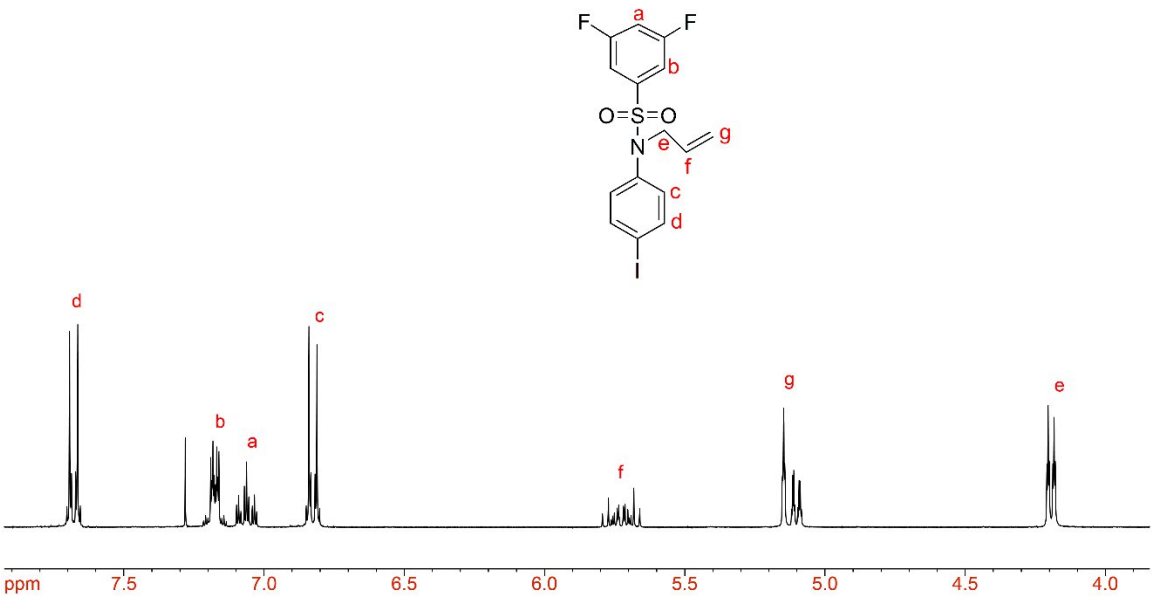


Figure 12. 300 MHz ^{1}H NMR spectrum ($CDCl_3$) of **1b**.

The ^{13}C NMR spectrum (**Figure 13**) contains eleven unique signals. It can be seen that there is some splitting of several signals, due to coupling with the fluorine atoms. Carbon **a** at 108.4 ppm appears as a triplet due to coupling with two equivalent *ortho* fluorines ($^{2}J_{C\text{-}F}$ = 24.99 Hz). Carbon **c** at 111.2 ppm gives rise to a doublet of doublets due to coupling with one *ortho* fluorine ($^{2}J_{C\text{-}F}$ = 28.10 Hz) and a *para* fluorine ($^{4}J_{C\text{-}F}$ = 8.87 Hz). Due to electron donation by the fluorine atoms in the *ortho* or *para* position, the signals for carbons **a** and **c** are shifted upfield. Carbon **d** at 141.6 ppm was identified as a triplet due to coupling with two *meta* fluorines with equivalent coupling constants ($^{3}J_{C\text{-}F}$ = 8.56 Hz). Carbon **b** at 160.9 ppm appears as a doublet of doublets due to coupling with the fluorine on the *ipso* carbon ($^{1}J_{C\text{-}F}$ = 243.8 Hz) and a *meta* fluorine ($^{3}J_{C\text{-}F}$ = 11.6 Hz). All of the remaining peaks in the spectrum appear as singlets.

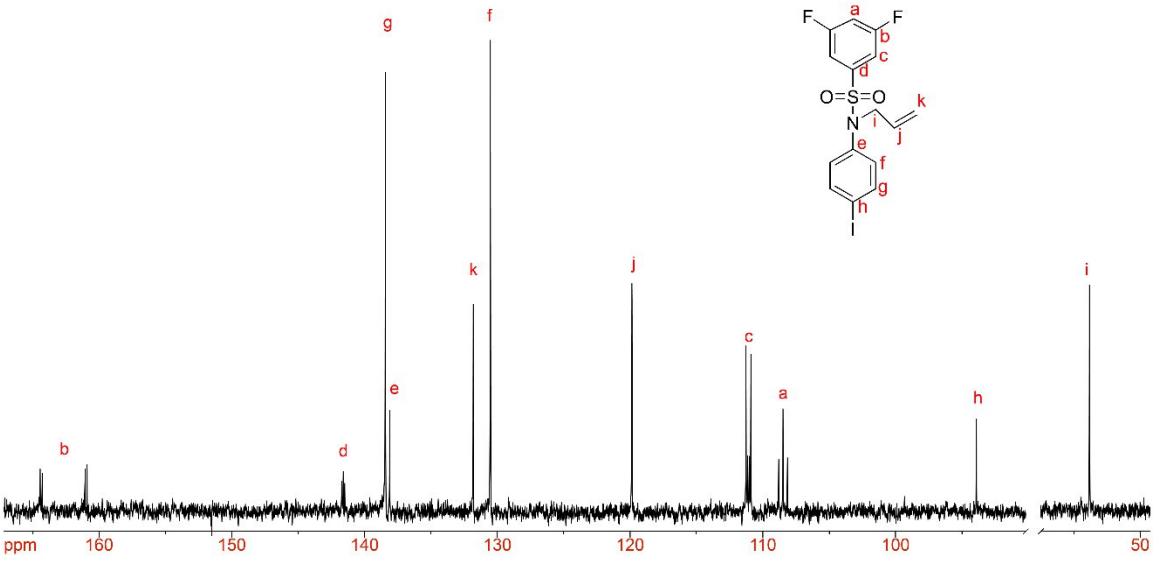


Figure 13. 75.5 MHz ^{13}C NMR spectrum ($CDCl_3$) of **1b**.

The ^{1}H and ^{13}C NMR spectra of compound **2b** are presented in **Figure 14** and **Figure 15**, respectively. There are nine unique peaks that appear in the ^{1}H NMR spectrum of **2b** (**Figure 14**). The most upfield proton **f**, at 1.40 ppm appears as triplet, proton **g** at 4.25 ppm gives rise to a doublet of triplets, proton **e** at 4.38 ppm was identified as quartet, all in the alkyl region, protons **h** and **i** appear as complex multiplets at 5.13 and 5.72 ppm, respectively. Proton **a**, at 7.05 ppm, gives rise to a triplet of triplets due to coupling with two fluorines with equivalent coupling constants ($^{3}J_{H\text{-}F}$ = 9.14 Hz) and two protons with equivalent coupling constants ($^{4}J_{H\text{-}H}$ = 2.32 Hz). Protons **b** and **c** at 7.17 ppm, appear as complex multiplets. Proton **d** at 8.01 ppm appears as a doublet.

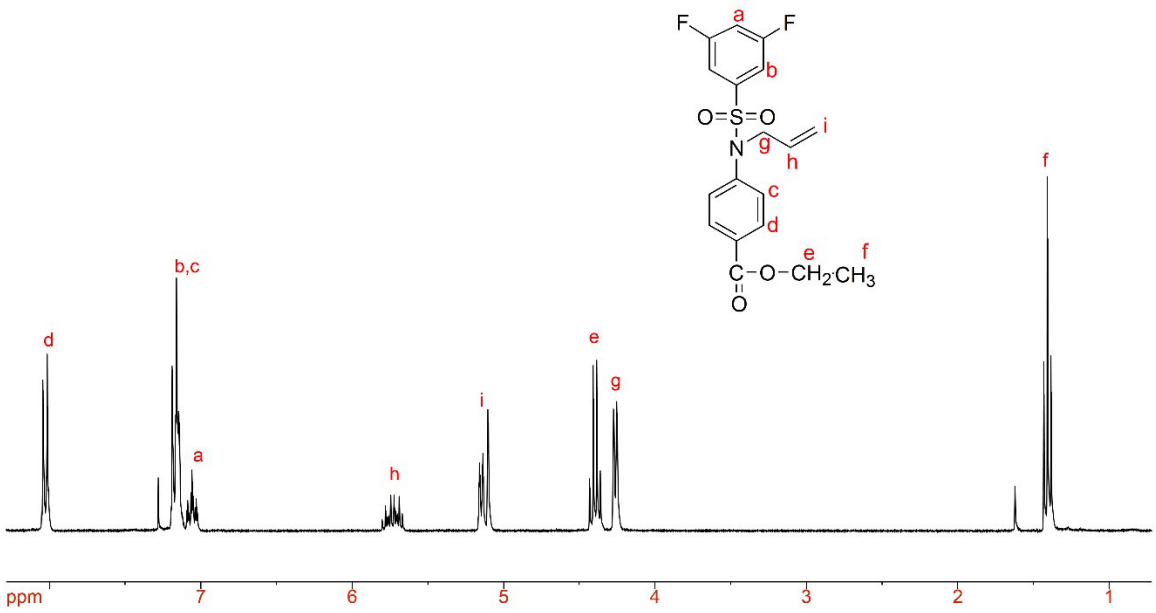


Figure 14. 300 MHz ^{1}H NMR spectrum ($CDCl_3$) of **2b**.

The ^{13}C NMR spectrum (**Figure 15)** contains fourteen unique signals. It can be seen that there is some splitting of several signals, due to coupling with the fluorine atoms. Carbon **a**, at 108.5 ppm, appears as a triplet due to coupling with two equivalent *ortho* fluorines ($^{2}J_{C\text{-}F}$ = 25.73 Hz). Carbon **c** at 110.8 ppm gives rise to a doublet of doublets due to coupling with one *ortho* fluorine ($^{2}J_{C\text{-}F}$ = 28.17 Hz) and a *para* fluorine ($^{3}J_{C\text{-}F}$ = 8.80 Hz). Due to electron donation by the fluorine atoms in the *ortho* or *para* position, signals for carbons **a** and **c** are shifted upfield. Carbon **d** at 141.5 ppm was identified as a triplet due to coupling with two *meta* fluorines with equivalent coupling constants ($^{3}J_{C\text{-}F}$ = 8.56 Hz). Carbon **b** at 161.0 ppm appears as a doublet of doublets due to coupling with the fluorine on the *ipso* carbon ($^{1}J_{C\text{-}F}$ = 252.2 Hz) and a *meta* fluorine ($^{3}J_{C\text{-}F}$ = 12.4 Hz). All of the remaining peaks in the spectrum are singlets.

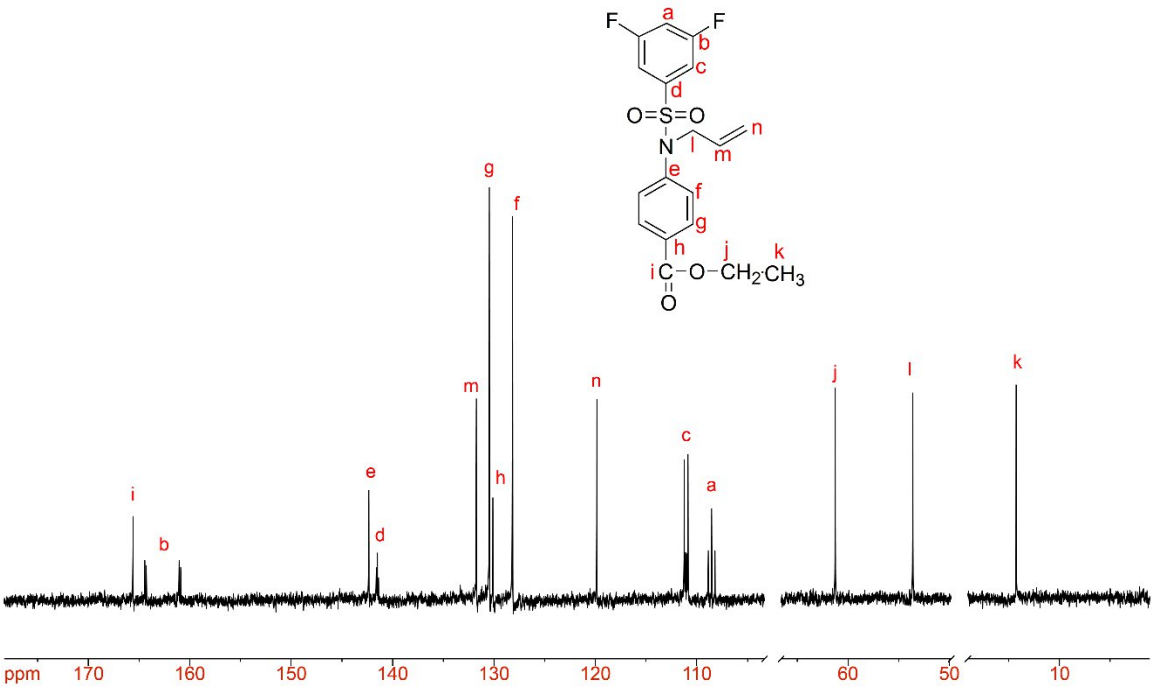


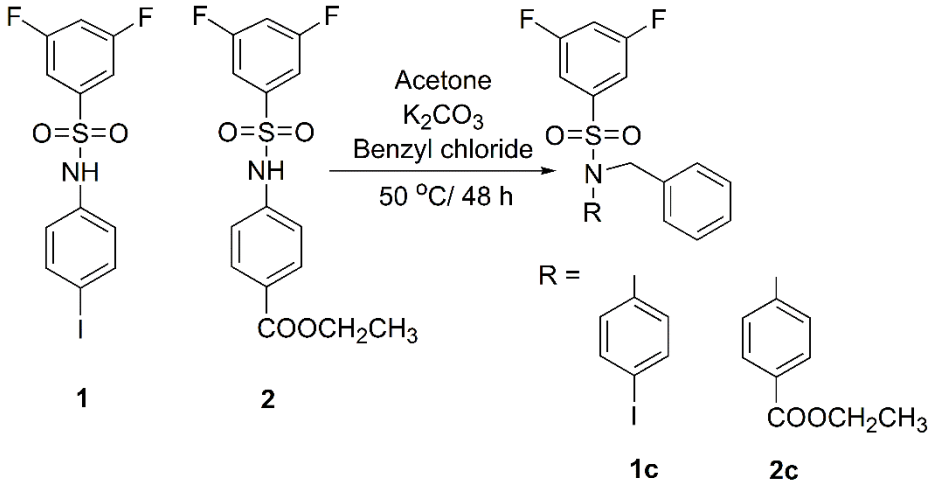
Figure 15. 75.5 MHz ^{13}C NMR spectrum ($CDCl_3$) of **2b**.

Synthesis of *N*-benzyl-*N*-(4-iodophenyl)-3,5-difluorobenzenesulfonamide (1c)

Synthesis of *N*-benzyl-*N*-(4-ethoxycarboxylphenyl)-3,5-difluorobenzenesulfonamide (2c)

The synthesis of *N*-benzyl-*N*-(4-iodophenyl)-3,5-difluorobenzenesulfonamide (**1c**) and *N*-benzyl-*N*-(4-ethoxycarboxylphenyl)-3,5-difluorobenzenesulfonamide (**2c**), respectively was achieved by benzylation of **1** and **2**, with benzyl chloride as shown in **Scheme 20.** In order to deprotonate the monomer **1** and **2,** potassium carbonate was used to form the nucleophile for S_N2 reactions with the benzyl chloride. The reaction mixtures were heated to 50 °C for 24 h at which point analysis by GC/MS confirmed conversion of the starting materials to the desired product. The product was obtained after work-up which involved diluting the reaction mixtures with chloroform, extraction with water,

evaporation to dryness, followed by recrystallization from methanol/water for **1c** and recrystallization from ethanol/water for **2c** . Both structures were confirmed by ^{1}H and ^{13}C NMR spectroscopy, GC/MS and elemental analysis.



Scheme 20. Synthesis of benzylated 3,5-difluorobenzene sulfonamides (**1c**) and (**2c**).

The ^{1}H and ^{13}C NMR spectra of compound **1c** are shown in **Figure 16** and **Figure 17,** respectively. There are eight unique peaks that appear in the ^{1}H NMR spectrum of **1c** (**Figure 16**) The most upfield proton **e** at 4.73 ppm gives rise to a singlet, proton **c** and proton **d,** at 6.73 and 7.57 ppm, respectively appear as doublets. Proton **a**, at 7.08 ppm, was identified as a triplet of triplets due to coupling with two fluorines with equivalent coupling constants ($^{3}J_{H\text{-}F}$ = 8.40 Hz) and two protons with equivalent coupling constants ($^{4}J_{H\text{-}H}$ = 2.31 Hz). Protons **b**, **f**, **g**, **h**, give rise to a series of broad over-lapping multiplets from 7.20- 7.27 ppm.

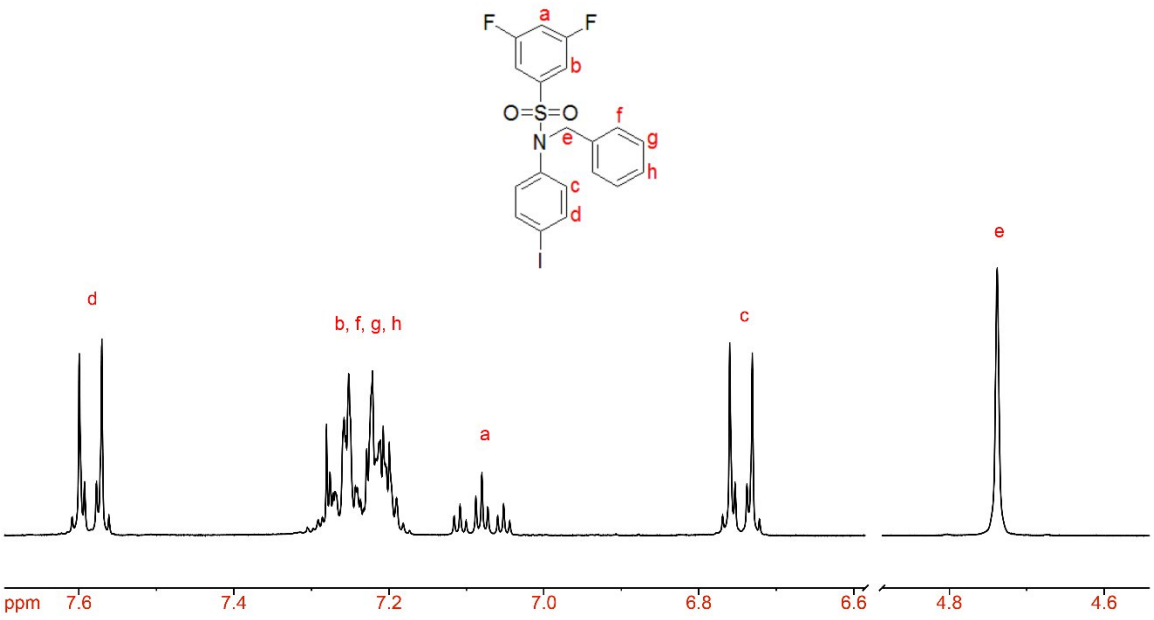


Figure 16. 300 MHz ^{1}H NMR spectrum ($CDCl_3$) of **1c**.

The ^{13}C NMR spectrum (**Figure 17**) contains thirteen unique signals. It can be seen that there is some splitting of several signals, due to coupling with the fluorine atoms. Carbon **a** at 108.5 ppm appears as a triplet due to coupling with two equivalent *ortho* fluorines ($^{2}J_{C\text{-}F}$ = 24.99 Hz). Carbon **c** at 110.9 ppm gives rise to a doublet of doublets due to coupling with one *ortho* fluorine ($^{2}J_{C\text{-}F}$ = 28.10 Hz) and a *para* fluorine ($^{4}J_{C\text{-}F}$ = 8.87 Hz). Due to electron donation by the fluorine atoms in the *ortho* or *para* position, signals for carbons **a** and **c** are shifted upfield. Carbon **d** at 141.7 ppm was identified as a triplet due to coupling with two *meta* fluorines with equivalent coupling constants ($^{3}J_{C\text{-}F}$ = 8.56 Hz). Carbon **b** at 161.0 ppm gives rise to a doublet of doublets due to coupling with the fluorine on the *ipso* carbon ($^{1}J_{C\text{-}F}$ = 243.8 Hz) and a *meta* fluorine ($^{3}J_{C\text{-}F}$ = 11.6 Hz). All of the remaining peaks in the spectrum appear as singlets.

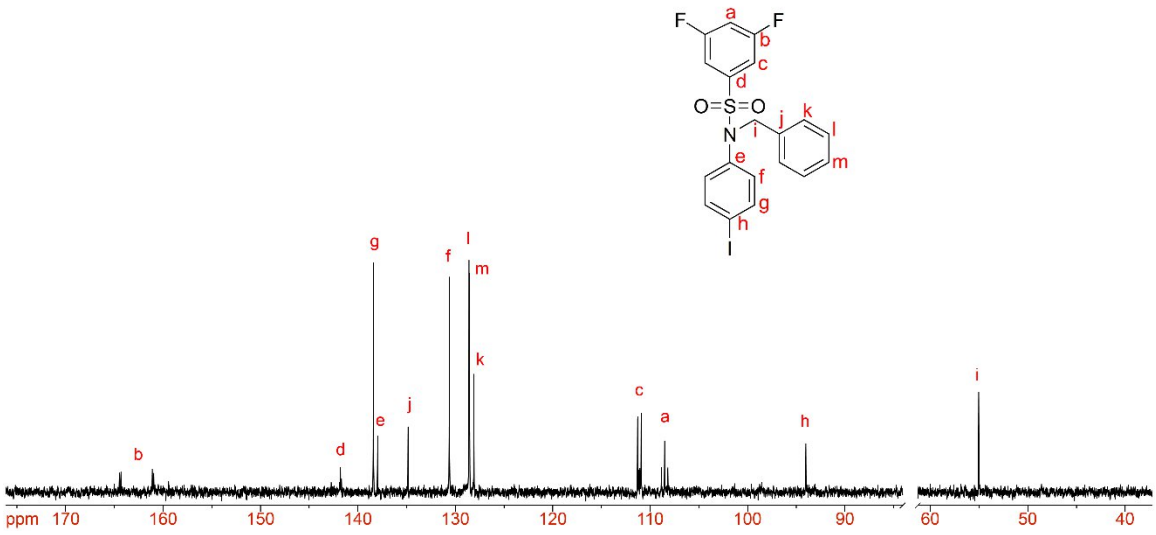


Figure 17. 75.5 MHz ^{13}C NMR spectrum ($CDCl_3$) of **1c**.

The ^{1}H and ^{13}C NMR spectra of compound **2c** are presented in **Figure 18** and **Figure 19**, respectively. There are ten unique peaks that appear in the ^{1}H NMR spectrum of **2c** (**Figure 18**). The most upfield proton **f**, at 1.38 ppm appears as triplet, proton **e** at 4.37 ppm appears as a quartet, proton **g** at 4.81 ppm gives rise to a singlet, all in the alkyl region. Proton **a** was identified as a triplet of triplets due to coupling with two fluorines with equivalent coupling constants ($^{3}J_{H\text{-}F}$ = 9.14 Hz) and two protons with equivalent coupling constants ($^{4}J_{H\text{-}H}$ = 2.32 Hz), over-lapping with proton **c** which gives rise to a doublet. Protons **b**, **h**, **i** and "**j**" appear as complex series of over-lapping multiplets between at 7.18 and 7.25 ppm. Proton **d** at 7.92 ppm gives rise to a doublet.

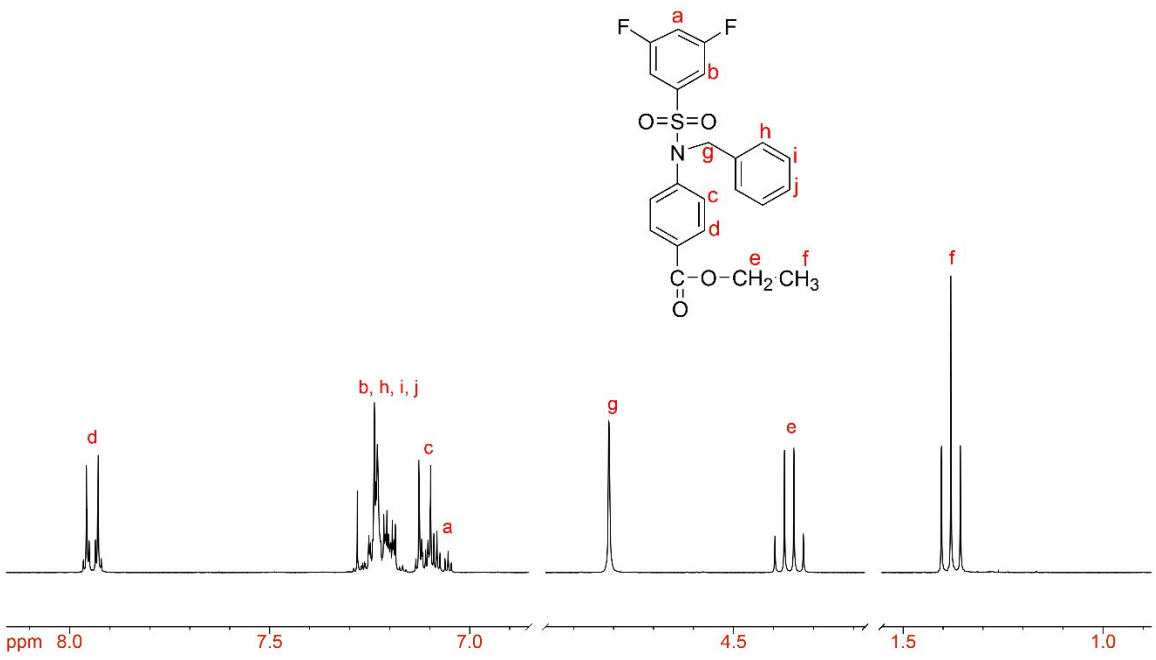


Figure 18. 300 MHz ^{1}H NMR spectrum ($CDCl_3$) of **2c**.

The ^{13}C NMR spectrum (**Figure 19**) contains sixteen unique signals. It can be seen that there is some splitting of several signals, due to coupling with the fluorine atoms. Carbon **a** at 108.6 ppm appears as a triplet due to coupling with two equivalent *ortho* fluorines ($^{2}J_{C\text{-}F}$ = 24.99 Hz). Carbon **c** at 110.9 ppm gives rise to a doublet of doublets due to coupling with one *ortho* fluorine ($^{2}J_{C\text{-}F}$ = 28.10 Hz) and a *para* fluorine ($^{4}J_{C\text{-}F}$ = 8.87 Hz). Due to electron donation by the fluorine atoms in the *ortho* or *para* position, signals for carbons **a** and **c** are shifted upfield. Carbon **d** at 141.6 ppm was identified as a triplet due to coupling with two *meta* fluorines with equivalent coupling constants ($^{3}J_{C\text{-}F}$ = 8.56 Hz). Carbon **b** at 161.1 ppm appears as a doublet of doublets due to coupling with the fluorine on the *ipso* carbon ($^{1}J_{C\text{-}F}$ = 243.82 Hz) and a *meta* fluorine ($^{3}J_{C\text{-}F}$ = 11.64 Hz). All of the remaining peaks in the spectrum are singlets.

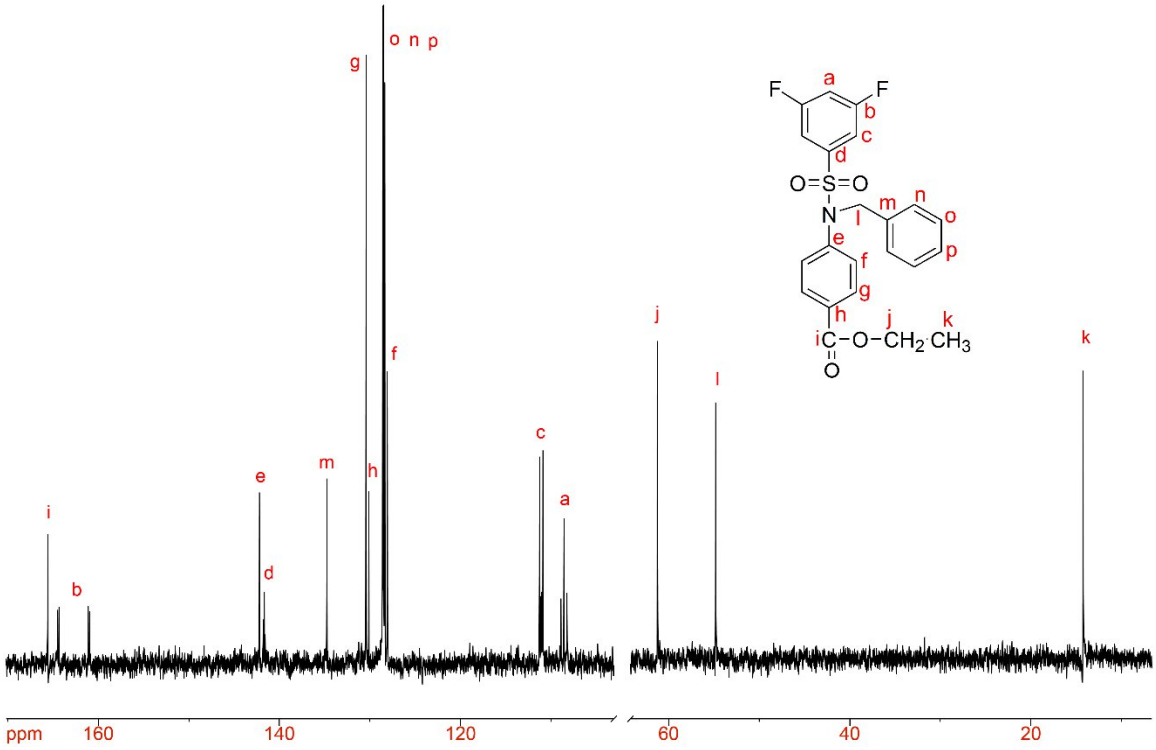
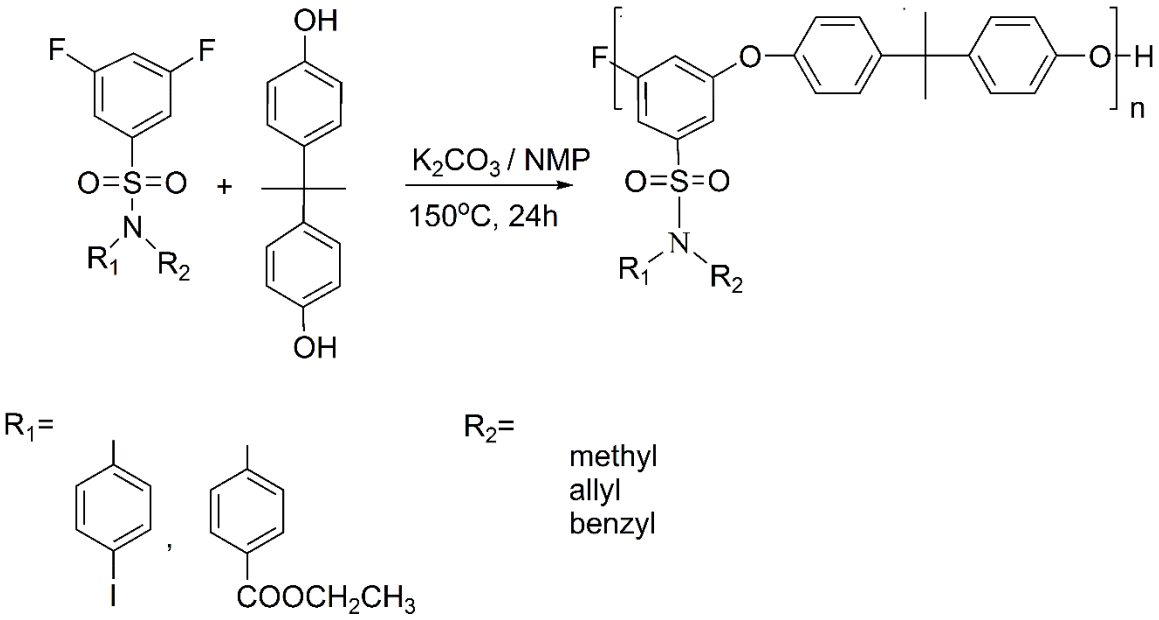


Figure 19. 75.5 MHz ^{13}C NMR spectrum ($CDCl_3$) of **2c**.

3.4. Homopolymer synthesis (3 a-c, 4 a-c)

Polymerization of 1a with Bisphenol-A to form 3a

Monomers **1a-c** and **2a-c** were converted to the corresponding PAEs **(3 a-c, 4 a-c)** by reaction of 3,5-Difluorobenzene sulfonamides with Bisphenol-A via NAS polycondensation reactions in the presence of K_2CO_3 in NMP at 150 °C for 24 hours (**Scheme 21**).



Scheme 21. Synthetic route for the preparation of homopolymers.

The polymers were precipitated from an excess of DI water and isolated by filtration to afford off white solids. In order to remove cyclic oligomers and other impurities the materials were reprecipitated from THF/ethanol or isopropanol (as noted in **Table 1** and **Table 2**).

The structures were confirmed by ^{1}H and ^{13}C NMR spectroscopy. The ^{13}C NMR spectrum of **3a** is shown in **Figure 20**. The spectrum indicates a successful displacement of both fluorine atoms and the iodo group being carried into the polymer (the C-I carbon signal is observed at 92.3 ppm). Carbons **a** and **d**, which appeared as triplets in the monomer at 108.6 and 140.5ppm, collapsed into singlets at 112.2 and 141.1 ppm, respectively. The two doublet of doublets in the fluorinated monomer, which represented carbons **b** and **c**, at 160.8 and 114.4 ppm, are also reduced to singlets at 159.3 and 110.5 ppm, respectively. In addition, 4 new signals from Bisphenol-A arise in the aromatic region, as well two new signals in the alkyl region.

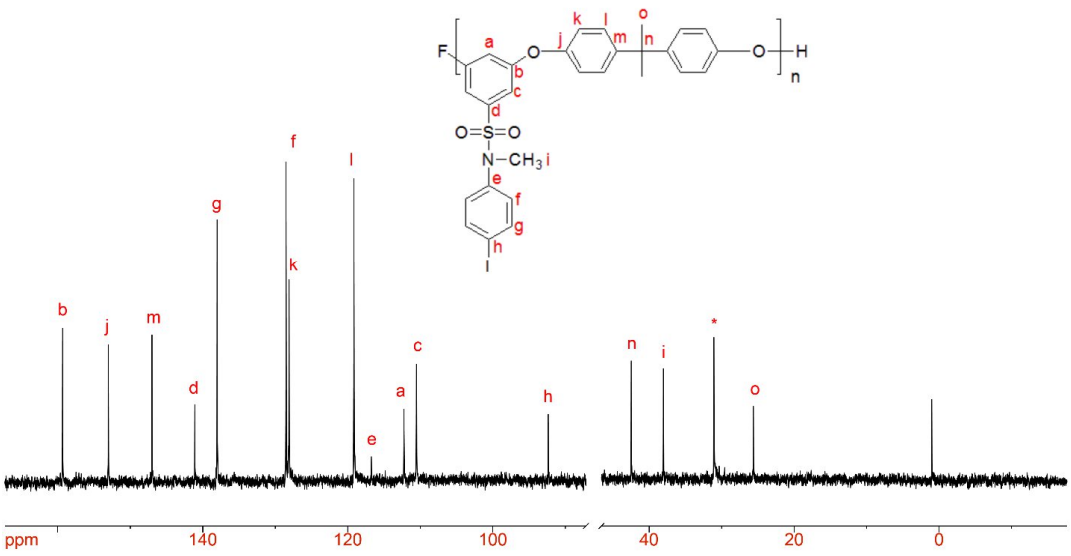


Figure 20. 75.5 MHz ^{13}C NMR spectrum ($CDCl_3$) of polymer **3a.**

As mentioned above, the ^{13}C NMR spectra in all of the *N*-(4-iodophenyl) homopolymers as shown in **Figure 21** indicate a successful displacement of both fluorine atoms and the iodo group being carried into the polymer (the C-I carbon signal is observed at 92.3 ppm, the chemical shifts are slightly shifted depending on the monomer). Signals for carbons **a** and **d** which appeared as triplets in the monomers, now are single peaks, and carbons **b** and **c** previously appearing as doublet of doublets collapsed into singlets. In addition, there are four signals in the aromatic region, as well as two in the alkyl region that arise from Bisphenol-A.

The major differences between the spectra are the specific signals arising from the monomers used. In *N*-methyl-*N*-(4-iodophenyl) homopolymer, **3a**, the methyl group is represented by a single peak at 42.4 ppm. In the *N*-allyl-*N*-(4-iodophenyl) homopolymer, **3b**, there are signals at 53.5, 119.4 and 132.2 ppm arising from the allyl moiety. As for

the *N*-benzyl-*N*-(4-iodophenyl) homopolymer, **3c**, benzyl group signals are observed at 54.6, 127.9, 128.5, 130.5 and 135.2 ppm.

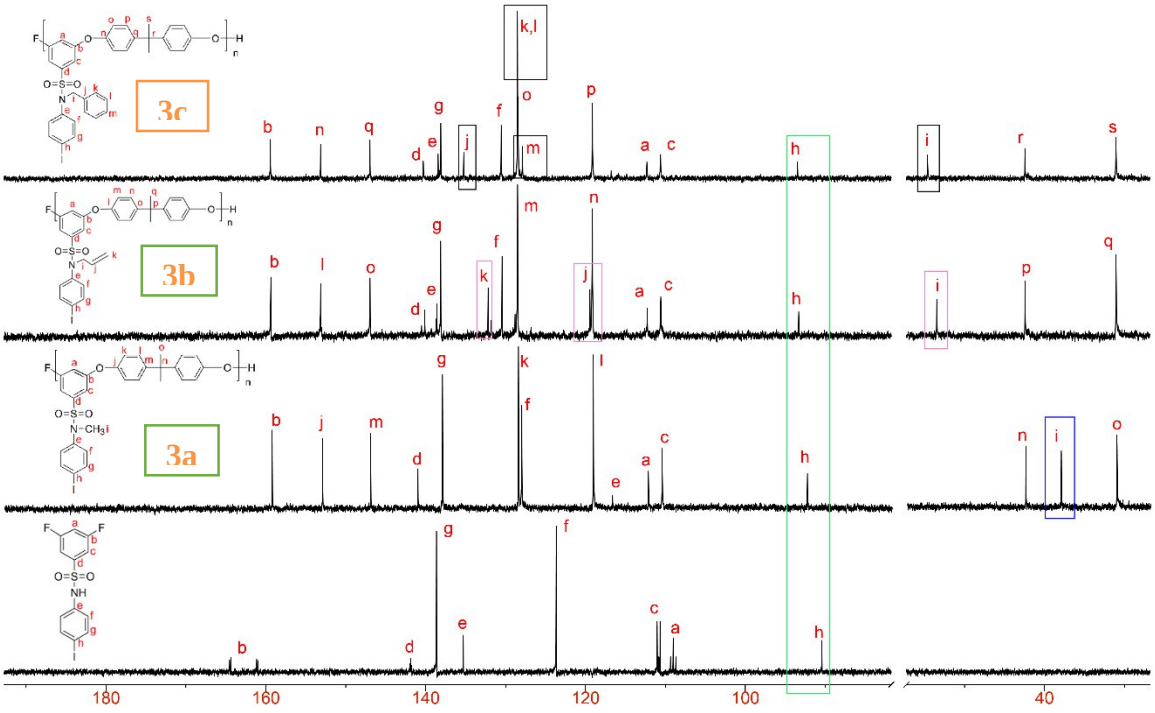


Figure 21. 75.5 MHz ^{13}C NMR spectra ($CDCl_3$) of *N*-(4-iodophenyl) homopolymers, **3a-c**.

Similarly to the *N*-(4-iodophenyl) homopolymers, the ^{13}C NMR spectra of *N*-(4-ethoxycarboxylphenyl) homopolymers as shown in **Figure 22** indicate a successful displacement of both fluorine atoms and the ester group being carried into the polymer (as expected, the ester carbonyl carbon signal is observed at 165.6 ppm, the chemical shifts are slightly shifted depending on the monomer). Signals for carbons **a** and **d** which appeared as triplets in the monomers, now are single peaks, and carbons **b** and **c** previously appearing as doublets of doublets, collapsed into singlets. In addition, there

are four signals in the aromatic region, as well as two in the alkyl region that arise from Bisphenol-A.

Likewise in the *N*-(4-iodophenyl) system, the major differences between the spectra are the specific signals arising from the monomers used; methyl, allyl and benzyl moieties.

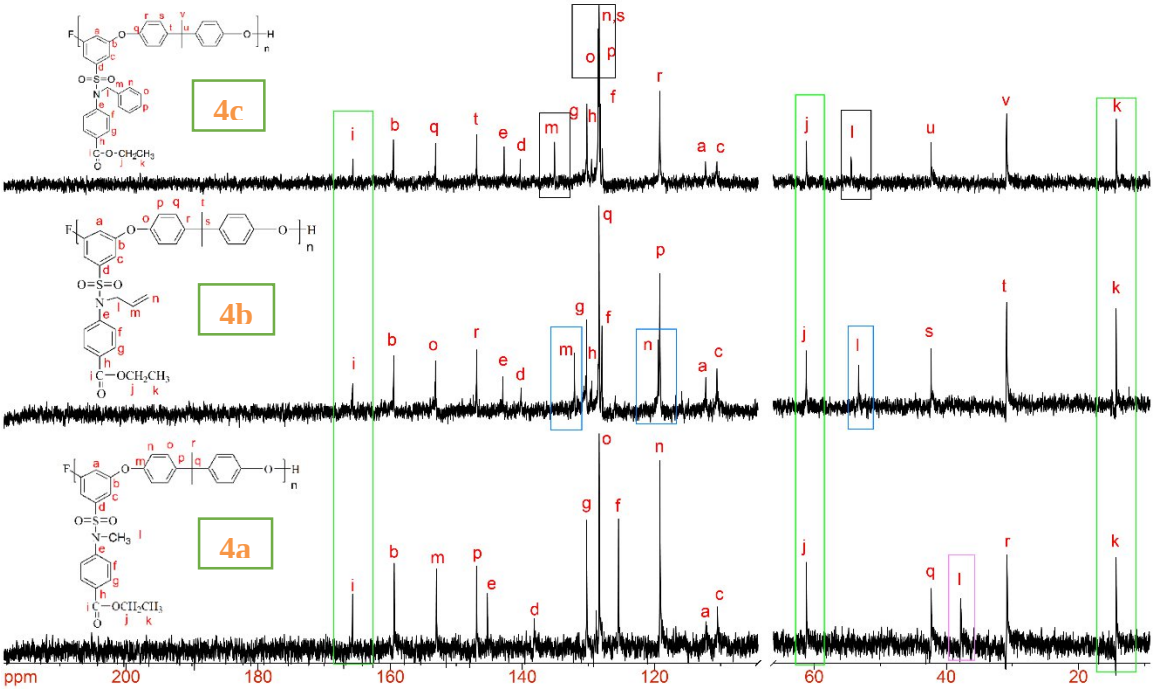
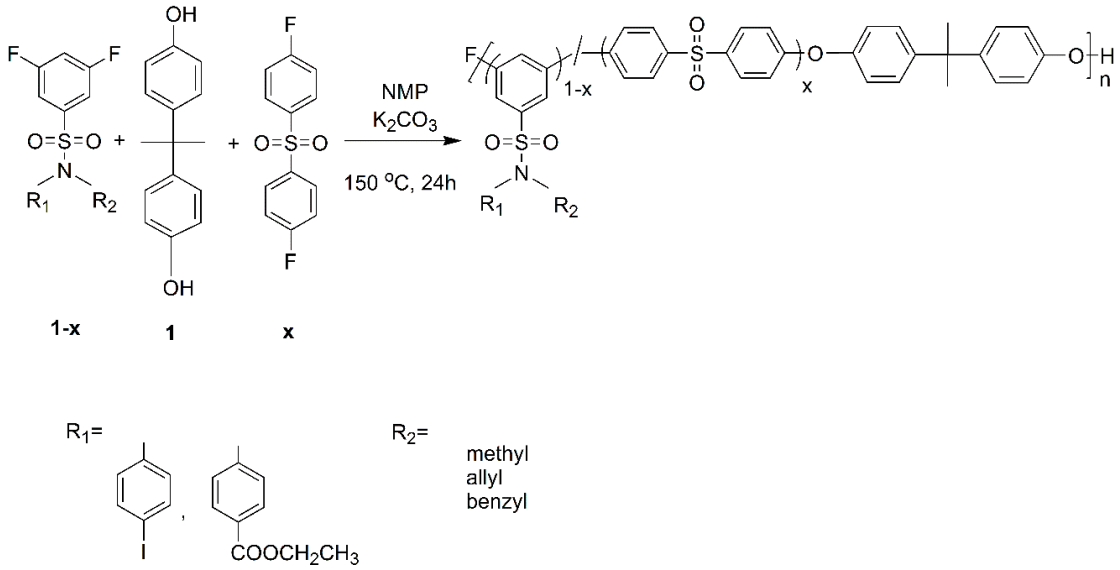


Figure 22. 75.5 MHz ^{13}C NMR spectra (CDCl3) of *N*-(4-ethoxycarboxylphenyl) homopolymers, **4a-c**

3.5. Random copolymer synthesis



Scheme 22. Synthetic route for the preparation of copolymers.

A series of PAEs with varying contents of the functional monomer ranging from 10 to 25 %, were prepared via a typical NAS polycondensation as illustrated in **Scheme 22**. Copolymers were prepared by incorporating specific amounts of the 3,5-difluorobenzene sulfonamide monomers **1a-c**, **2a-c** and 4,4-difluorodiphenylsulfone. Successful incorporation of monomers into the polymers was confirmed by ^{13}C DEPT 90 NMR spectroscopy. An overlay of the ^{13}C DEPT 90 NMR spectrum of the homopolymer **3a** and the copolymers **5a** and **5b** with 25 and 10 % of monomer is shown in **Figure 23**.

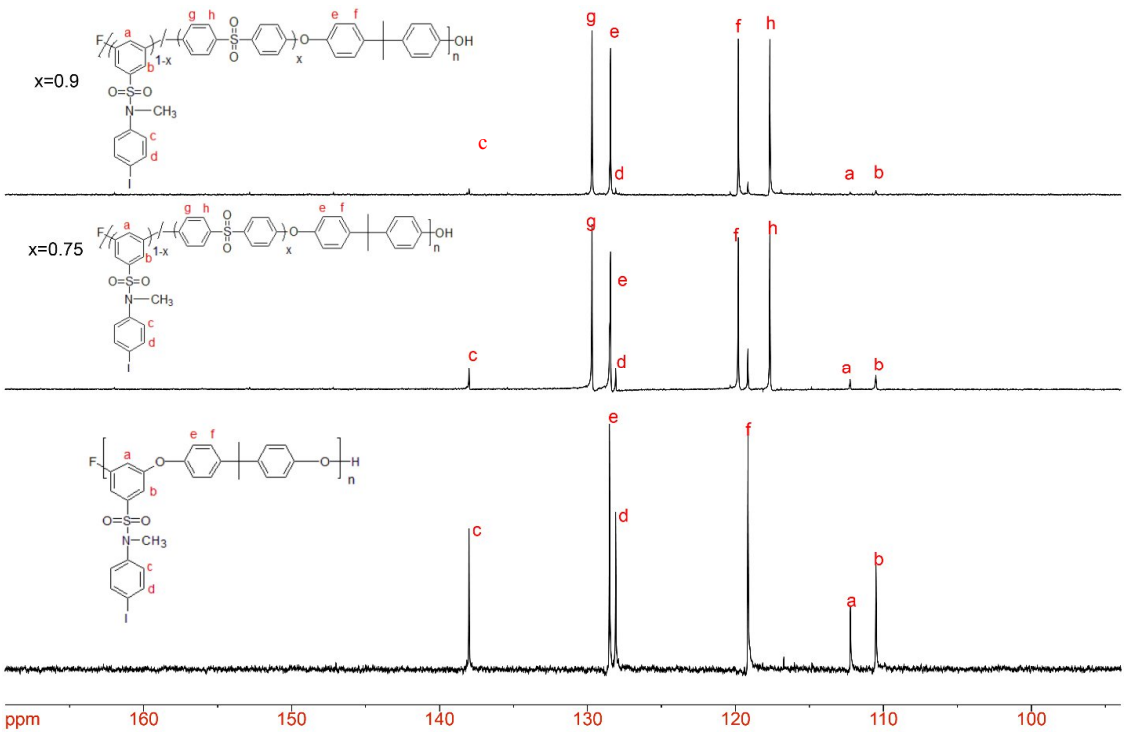


Figure 23. Overlay ^{13}C DEPT 90 NMR (DMSO-d6) of **3a** homopolymer and **5a** and **5b** copolymers.

The ^{13}C DEPT 90 NMR spectrum of **5a** confirms that the CH signals observed for homopolymer **3a** are still present, additionally signals that represent the CH groups of the 4,4`-diphenylsulfone rings are now present in the copolymer. In all of the polymers the intensity of CH signals **a**, **b**, **c**, **d** arising from the sulfonamide decreased in intensity in the 25 and 10 % ratio of sulfonamide monomer, while signals **g**, **h** arising from the diphenylsulfone ring increased accordingly. Bisphenol-A signals remained constant with slight changes in chemical shifts depending on the sulfonamide monomer.

3.6. Polymer molecular weight and thermal properties

The polymers were further analyzed utilizing Size exclusion chromatography (SEC), Thermogravimetric analysis (TGA) and Differential scanning calorimetry (DSC). Characterization data, including molecular weight (M_w), polydispersity index (PDI) and percent yield (%) are summarized in **Table 1** and **Table 2**.

Table 1. Molecular weight, PDI and % yields for *N*-(4-iodophenyl) polymers.

Polymer	% yield	M_w (Da)	PDI	Reprecipitating solvent
3a, *N*-methyl-*N*-(4-iodophenyl) 100%	82	22 400	2.14	Ethanol
5a, *N*-methyl-*N*-(4-iodophenyl) 25%	71	37 200	2.2	Isopropanol
5b, *N*-methyl-*N*-(4-iodophenyl) 10%	79	29 700	2.5	Isopropanol
3b, *N*-allyl-*N*-(4-iodophenyl) 100%	52	16 100	2.5	Isopropanol
6a, *N*-allyl-*N*-(4-iodophenyl) 25%	77	22 300	2.54	Isopropanol
6b, *N*-allyl-*N*-(4-iodophenyl) 10%	64	25 700	2.6	Isopropanol
3c, *N*-benzyl-*N*-(4-iodophenyl) 100%	68	10 200	1.8	Isopropanol
7a, *N*-benzyl-*N*-(4-iodophenyl) 25%	77	8 400	1.84	Isopropanol
7b, *N*-benzyl-*N*-(4-iodophenyl) 10%	88	32 700	2.1	Isopropanol

Table 2. Molecular weight, PDI and % yields for *N*-(4-ethoxycarboxylphenyl) polymers.

Polymer	% yield	M_w	PDI	Reprecipitating solvent
4a, *N*-methyl-*N*-(4-ethoxycarboxylphenyl) 100%	32	20 600	1.7	Isopropanol
8a, *N*-methyl-*N*-(4-ethoxycarboxylphenyl) 25%	77	41 700	2.2	Ethanol
8b, *N*-methyl-*N*-(4-ethoxycarboxylphenyl) 10%	77	24 000	2.3	Ethanol
4b, *N*-allyl-*N*-(4-ethoxycarboxylphenyl) 100%	16	6 300	1.54	Isopropanol
9a, *N*-allyl-*N*-(4-ethoxycarboxylphenyl) 25%	56	17 700	2.2	Ethanol
9b, *N*-allyl-*N*-(4-ethoxycarboxylphenyl) 10%	65	28 400	2.3	Ethanol
4c, *N*-benzyl-*N*-(4-ethoxycarboxylphenyl) 100%	36	5 800	1.4	Isopropanol
10a, *N*-benzyl-*N*-(4-ethoxycarboxylphenyl) 25%	50	12 600	2.0	Ethanol
10b, *N*-benzyl-*N*-(4-ethoxycarboxylphenyl) 10%	64	24 100	2.7	Ethanol

Size exclusion chromatography was used to determine molecular weight and molecular weight distributions of polymers soluble in THF/5% acetic acid. Polydispersity index (PDI) and weight average molecular weight were determined using the refractive index (RI) and light scattering detectors. The weight average molecular weights were found to be from 5,800 to 41,700 Daltons with PDI values from 1.4 to 2.7. In both *N*-(4-iodophenyl) and *N*-(4-ethoxycarboxylphenyl) series, methyl functionalized polymers afforded the highest M_w polymers, whereas in the *N*-(4-ethoxycarboxylphenyl) series it can be noticed that the M_w values increase as the % of the sulfonamide moiety decreases.

The thermal stability of the polymers, reported as 5 % decomposition temperature ($T_{d5\%}$) under nitrogen was investigated using Thermogravimetric analysis (TGA), while glass transition temperatures (T_g) were determined using Differential Scanning Calorimetry (DSC). Characterization data, including glass transition temperature (T_g), 5 % decomposition temperature ($T_{d5\%}$), first step percentage loss observed, as well as calculated weight loss percentages are summarized in **Table 3** and **Table 4**.

Table 3. Thermal data for *N*-(4-iodophenyl) polymers.

Polymer	**T_g (^oC)**	**$T_{d\,5\%}$ (^oC)**	**1st Step % loss**	**Weight % NR_1R_2**
3a, *N*-methyl-*N*-(4-iodophenyl) 100%	112	363	38.8	38.7
5a, *N*-methyl-*N*-(4-iodophenyl) 25%	170	395	9.80	12.0
5b, *N*-methyl-*N*-(4-iodophenyl) 10%	180	446	3.7	5
3b, *N*-allyl-*N*-(4-iodophenyl) 100%	123	350	42.0	41.2
6a, *N*-allyl-*N*-(4-iodophenyl) 25%	164	362	8.3	14.7
6b, *N*-allyl-*N*-(4-iodophenyl) 10%	177	432	3.6	6.3
3c, *N*-benzyl-*N*-(4-iodophenyl) 100%	123	303	41.6	43.5
7a, *N*-benzyl-*N*-(4-iodophenyl) 25%	145	343	11.3	14.7
7b, *N*-benzyl-*N*-(4-iodophenyl) 10%	178	442	4.5	6.3

Table 4. Thermal data for *N*-(4-ethoxycarboxylphenyl) polymers.

Polymer	T_g (^oC)	$T_{d\ 5\%}$ (N_2)	1st Step % loss	Weight %
4a, *N*-methyl-*N*-(4-ethoxycarboxylphenyl) 100%	138	379	31.6	32.6
8a, *N*-methyl-*N*-(4-ethoxycarboxylphenyl) 25%	170	404	7.6	9.4
8b, *N*-methyl-*N*-(4-ethoxycarboxylphenyl) 10%	181	444	3.5	4.0
4b, *N*-allyl-*N*-(4-ethoxycarboxylphenyl) 100%	107	324	33.3	35.7
9a, *N*-allyl-*N*-(4-ethoxycarboxylphenyl) 25%	167	368	6.0	10.8
9b, *N*-allyl-*N*-(4-ethoxycarboxylphenyl) 10%	177	415	1.9	4.40
4c, *N*-benzyl-*N*-(4-ethoxycarboxylphenyl) 100%	124	362	31.6	40.8
10a, *N*-benzyl-*N*-(4-ethoxycarboxylphenyl) 25%	172	393	7.1	12.97
10b, *N*-benzyl-*N*-(4-ethoxycarboxylphenyl) 10%	184	418	3.6	5.5

Polymers displayed moderate thermal stability above 340 °C (with the exception of **3b**), under nitrogen atmosphere. The 5% degradation temperature for the first degradation step was from 340 °C for **3b** to 446 °C for **5b.**

The TGA thermogram of polymer **3c**, under nitrogen atmosphere is shown in **Figure 24** and clearly show two distinct degradation steps. The first degradation step is assigned to the loss of the *N*-benzyl-*N*-(4-iodophenyl). This has been concluded based on the theoretical percentage weight loss values calculated for the *N*-benzyl-*N*-(4-iodophenyl) moiety which were close to the experimental value. The theoretical value was 43.5 % while the observed value was 41.6 %. The TGA data for the polymers are listed in **Table 2** and **Table 3**.

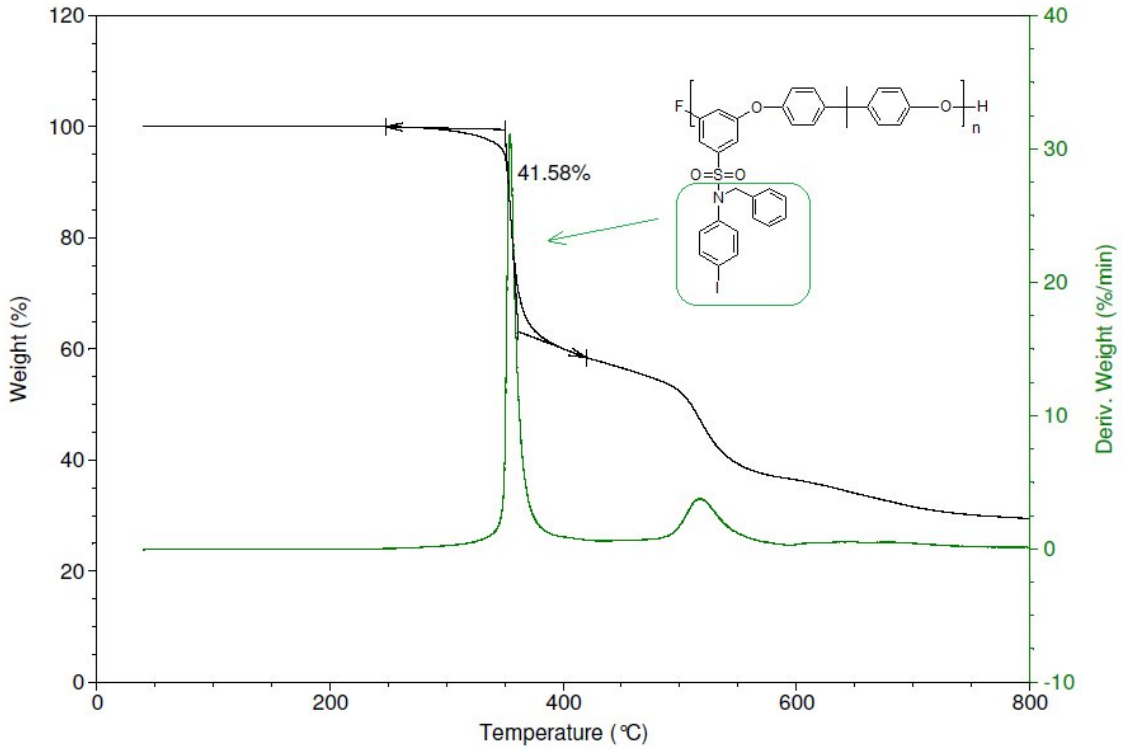


Figure 24. TGA trace of *N*-benzyl-*N*-(4-iodophenyl), **3c** under nitrogen.

As mentioned above, the TGA thermograms clearly show two distinct degradation steps as shown in **Figure 25,** where it can also be seen that as the ratio of the sulfonamide monomer in the polymers decreases, so does the first degradation step which is assigned the loss of the *N*-methyl-*N*-(4-ethoxycarboxylphenyl) group.

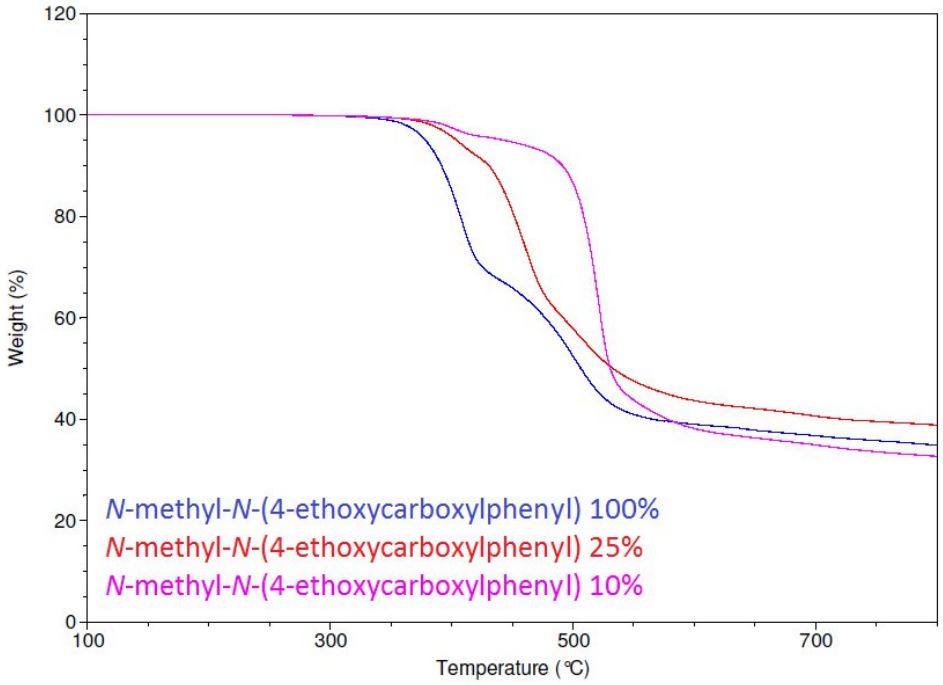


Figure 25. TGA traces of *N*-methyl-*N*-(4-ethoxycarboxylphenyl) polymers under nitrogen.

Glass transition temperatures (T_g) were determined using Differential Scanning Calorimetry (DSC) and overlays of the DSC traces of selected *N*-(4-iodophenyl) and *N*-(4-ethoxycarboxylphenyl) polymers are shown in **Figure 26** and **Figure 27**.

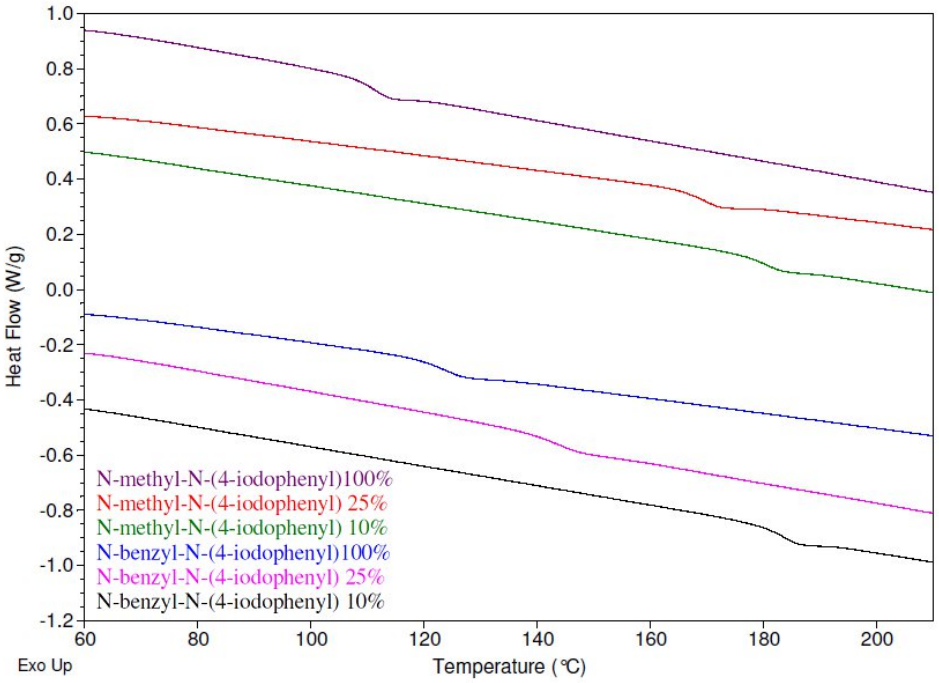


Figure 26. DSC traces for *N*-(4-iodophenyl) polymers.

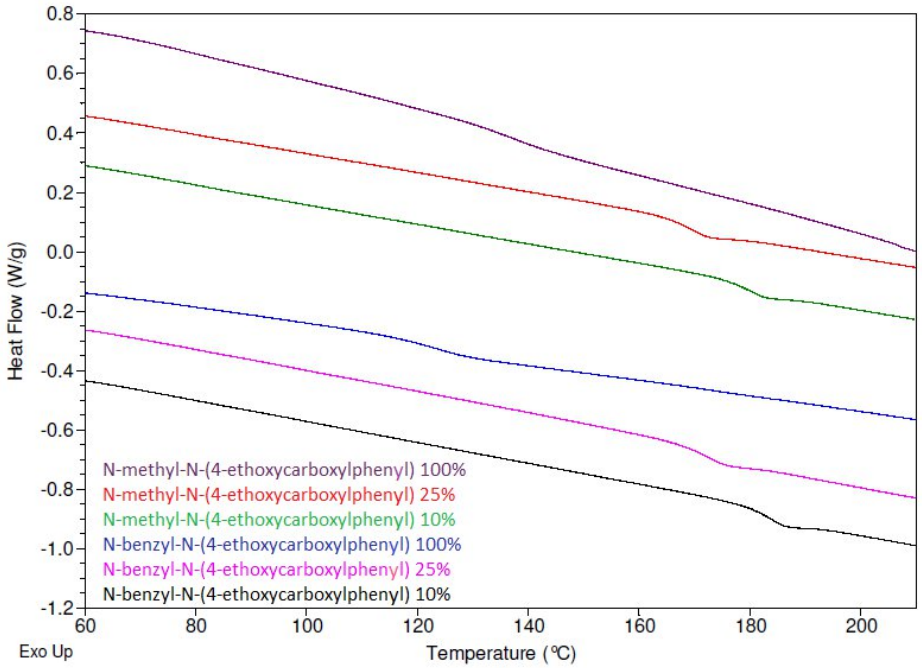


Figure 27. DSC traces for *N*-(4-ethoxycarboxylphenyl) polymers.

The glass transition temperatures ranged from 112 °C to 184 °C. The higher T_g can be attributed to a more rigid polymer backbone, making it more difficult for the polymer to rotate around the sigma bonds. For example, the *N*-methyl-*N*-(4-iodophenyl) homopolymer displayed a T_g value of 112 °C, whereas the 25% monomer ratio in the copolymer possessed an increase of T_g to 170°C and the 10% monomer ratio in the copolymer provided the highest T_g of 180 °C. In other words, as the diphenylsulfone moiety in the polymer was increased, so did the T_g. Additionally, the traces provide insight into amorphous structure of the polymers since neither a melting nor crystallization transitions were observed. The same trend can be noticed for all of the polymer series as shown in **Table 3** and **Table 4**.

4. CONCLUSION

A series of 3,5-difluorobenzene sulfonamides bearing combinations of aryl iodide, alkyl, allyl, 4-ethoxycarboxylphenyl and benzyl moieties was successfully synthesized and converted to the corresponding PAEs by reaction with Bisphenol-A, via a typical NAS polycondensation. Copolymers with varying contents of the functional monomer, ranging from 10 to 25 %, were also prepared.

The weight average molecular weights, as determined by SEC analysis, ranged from 5,800 to 41,700 Da, with PDI values from 1.4 to 2.7.

Thermal properties for the resulting polymers were determined by TGA and DSC with TGA analysis showing the polymers possessed moderate thermal stability above 340 °C (with the exception of *N*-benzyl-*N*-(4-iodophenyl) homopolymer, **3c**) with the 5% degradation temperature from 340 °C for *N*-allyl-*N*-(4-iodophenyl) homopolymer, **3b** to 446 °C for *N*-methyl-*N*-(4-iodophenyl) 10%, **5b.**

DSC showed that all the polymers were amorphous with glass transition temperatures ranging from a low of 112 °C for *N*-methyl-*N*-(4-iodophenyl) homopolymer, **3a** to a high of 184 °C for *N*-benzyl-*N*-(4-ethoxycarboxylphenyl) 10%, **10b**. As expected, PAEs with the highest content of the functional monomer had the lowest T_g value, due to the less rigid polymer chains, allowing segments to rotate more easily.

5. FUTURE WORK

Polymers carrying pendent iodo group, as well as the *N*-allyl-*N*-(4-ethoxycarboxylphenyl) polymers can undergo further modification via post polymerization modification chemistry, such as Stille coupling and thiol-ene reactions. Post modification of the iodo polymers with styrene could give rise to light switchable stilbene materials, while the allyl group could undergo addition reactions, serving as potential cross-linking sites.

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