PREPARATION OF PERFLUORINATED IONOMERS FOR FUEL CELL APPLICATIONS

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ABSTRACT

One of the major issues with the current membrane technology for polymer electrolyte membrane fuel cells is the low conductivity seen at low relative humidity. This dissertation discloses the preparation of perfluorinated polymers with higher densities of acid sites and higher conductivities to overcome this issue. These materials are prepared using a system designed to safely synthesize and polymerize tetrafluoroethylene (TFE) on a hundred gram scale.

The copolymerization of TFE and perfluoro-2-(2-fluorosulfonylethoxy) propyl vinyl ether (PSEPVE) to prepare materials with varying ratios of the two monomers was carried out by solution, bulk, and emulsion polymerization techniques. Additionally, the homopolymer of PSEPVE has been prepared and characterized by MALDI-TOF mass spectrometry, which shows the low molecular weight distribution seen in other similar materials in the literature is due to a high rate of β-scission termination. Spectroscopic measurements and thermal analysis were carried out on these samples to obtain better characterization than was currently available.

Producing polymers with a higher amount of PSEPVE, and thus higher density of acid sites, leads to the materials becoming water soluble after hydrolysis. However, addition of a curable ter-monomer allows the polymer chains to be crosslinked to regain water insolubility. Using this approach, water insoluble membranes with high densities of acid sites and conductivities up to 5.5 times higher than Nafion® 115, the standard benchmark for fuel cell membranes, have been produced.

Preparation of high molecular weight, low EW copolymers of TFE and PSEPVE is difficult due to the reactivity ratios of the two monomers. Literature reactivity ratios for VDF and PSEPVE are more favorable for preparation of high molecular weight, low EW copolymers. Here, alternating copolymers of VDF and PSEPVE are prepared for the first time; where high molecular weight samples have been shown to possess low swelling characteristics in water. It has also been found the lower molecular weight samples that are soluble in perfluorohexane can be converted to perfluorinated polymers by direct fluorination with 20% elemental fluorine in nitrogen with 254 nm UV irradiation.

The author makes no warranties, expressed or implied, and assumes no liability in connection with any use of the information presented in this dissertation. No one but persons having technical skill in this area of fluorine chemistry should attempt or repeat anything presented herein, and then at their own discretion and risk.

DEDICATION

This dissertation is dedicated to my wife, Franchessa Sayler, for her love, support, and advice during this work. She has enriched my life in more ways than she knows and filled it with purpose and love.

I would also like to dedicate this dissertation to my mother, Kathy Sayler, and grandparents, Hunter and Jean Read, for their love through the years and support in helping me to continue my education.

LIST OF ABBREVIATIONS AND SYMBOLS

˚C	degrees Celsius
δ	chemical shift in parts per million
3M monomer	perfluoro-4-(fluorosulfonyl) butyl vinyl ether, $(CF_2=CFOCF_2CF_2CF_2CF_2SO_2F)$
3P	bis(pentafluoropropionyl) peroxide, $(CF_3CF_2C(O)OOC(O)CF_2CF_3)$
4P	bis(heptafluorobutyryl) peroxide, $(CF_3CF_2CF_2C(O)OOC(O)CF_2CF_2CF_3)$
8CNVE	perfluoro 8-cyano-5-methyl-3,6-dioxa-1-octene, $(CF_2=CFOCF(CF_3)CF_2OCF_2CF_2CN)$
ARC®	accelerating rate calorimeter
ATR	attenuated total reflectance
β_{PS}	$HO_3SCF_2CF_2OCF(CF_3)CF_2$- radical or end group
b.p.	boiling point
BPR	back pressure regulator
CMC	critical micelle concentration
DHB	2,5-dihydroxybenzoic acid, $[C_6H_3(CO_2H)(OH)_2]$
DMSO	dimethyl sulfoxide
DP	HFPO dimer peroxide end group, $CF_3CF_2CF_2O(CF_3)CF$-
DuPont	E. I. du Pont de Nemours and Co.
Dow	perfluoro-3-oxa-4-pentene sulfonyl fluoride, $(CF_2=CFOCF_2CF_2SO_2F)$
DSC	differential scanning calorimetry
ePTFE	expanded polytetrafluoroethylene, e-$(-CF_2-CF_2-)_n$
ETFE	ethylene tetrafluoroethylene copolymer, $(-CH_2CH_2CF_2CF_2-)_n$
EW	equivalent weight, grams of polymer needed to have 1 mole of acid sites

FT-IR	Fourier transform infrared spectroscopy
FEP	fluorinated ethylene propylene, $(\text{-}CF_2CF_2)_m\text{-}(CF_2CF(CF_3)\text{-})_n$
g	grams
HFC 43-10	2,3-dihydrodecafluoropentane, $(CF_3CFHCFHCF_2CF_3)$
HFE 7100	methyl nonafluorobutyl ether, $(CH_3\text{-}O\text{-}CF_2CF_2CF_2CF_3)$
HFP	hexafluoropropylene, $(CF_2{=}CF(CF_3))$
HFPOdaf	hexafluoropropylene oxide dimer acid fluoride, $(CF_3CF_2CF_2O(CF_3)CFC(O)F)$
HFPOdp	hexafluoropropylene oxide dimer peroxide, $[CF_3CF_2CF_2O(CF_3)CFC(O)O\text{-}]_2$
K	Kelvin
k	rate constant
KHP	potassium hydrogen phthalate, $C_6H_4(CO_2H)(CO_2^- K^+)$
L	liters
M	molarity
M1	monomer 1
M2	monomer 2
M_n	number average molecular weight
M_w	weight average molecular weight
MAFS-010	Merck advanced fluorosurfactant 010 - bis(perfluorobutyl) phosphinic acid, $(C_4F_9)_2P(O)OH$
MALDI-TOF	matrix assisted laser desorption ionization - time of flight
MEA	membrane electrode assembly
mil	milliinch
MS	mass spectrometry

mS	millisiemens
NMR	nuclear magnetic resonance
N117	Nafion$^{®}$ membrane with equivalent weight of 1100 and thickness of 7 milliinches
PDI	polydispersity index
PE	polyethylene, $(\text{-CH}_2\text{CH}_2\text{-})_n$
PEMFC	polymer electrolyte membrane fuel cell
PFIB	perfluoroisobutylene, $[(\text{CF}_3)_2\text{C=CF}_2]$
PFOA	ammonium perfluorooctanoate, $(\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CO}_2^{-}\ \text{NH}_4^{+})$
PFA	perfluoroalkoxy resin, $(\text{-CF}_2\text{CF}_2\text{-})_m(\text{-CF}_2\text{CF(OR}_f\text{)-})_n$
PFPA	pentafluoropropionic acid, $(\text{CF}_3\text{CF}_2\text{CO}_2\text{H})$
ppm	parts per million
psia	pounds per square inch absolute
psig	pounds per square inch gauge
PTFE	polytetrafluoroethylene, $(\text{-CF}_2\text{-CF}_2\text{-})_n$
PVDF	polyvinylidene difluoride, $(\text{-CF}_2\text{-CH}_2\text{-})_n$
R113	1,1,2-trichloro-1,2,2-trifluoroethane, $\text{CCl}_2\text{F-CF}_2\text{C}$
R22	chlorodifluoromethane, CClF_2H
R_f	perfluoroalkyl
RH	relative humidity
rpm	rotations per minute
SEC	size-exclusion chromatography
SEM	scanning electron microscopy
T_d	decomposition temperature (5 percent weight loss)

TFA	trifluoroacetic acid, ($CF_3C(O)OH$)
TFE	tetrafluoroethylene, ($CF_2=CF_2$)
TGA	thermal gravimetric analysis
UAXD	Copolymer of TFE and Dow (University of Alabama eXperimental Dow resin)
UAXDC	Terpolymer resin of Dow, TFE, and 8CNVE
UAXDC#C	Cured terpolymer of Dow, TFE, and 8CNVE
UAXDH	Dow homopolymer (University of Alabama eXperimental Dow Homopolymer)
UAXH	PSEPVE homopolymer (University of Alabama eXperimental Homopolymer)
UAXH#A	Sulfonamide resin of PSEPVE homopolymer
UAXH#H	Hydrolyzed resin of PSEPVE homopolymer
UAXHC	Copolymer of PSEPVE and 8CNVE
UAXHC#C	Cured copolymer of PSEPVE and 8CNVE
UAXR	Copolymer of TFE and PSEPVE (University of Alabama eXperimental Resin)
UAXRA	Sulfonamide resin of TFE and PSEPVE copolymer
UAXV	Copolymer of VDF and PSEPVE
VDF	vinylidene difluoride, ($CH_2=CF_2$)

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CHAPTER 1

SYNTHESIS OF TETRAFLUOROETHYLENE AND DESIGN AND OPERATION OF A SYSTEM TO SAFELY POLYMERIZE TETRAFLUOROETHYLENE

1.1 Introduction to TFE and Fluoropolymers

Tetrafluoroethylene (TFE) is a valuable building block in the chemical industry, specifically in the preparation of fluoropolymers. Since the serendipitous discovery of polytetrafluoroethylene (PTFE) in 1938 by Dr. Roy J. Plunkett while attempting to synthesize new chlorofluorocarbons at E. I. du Pont de Nemours and Company (DuPont), fluoropolymers have been important materials. Shortly after its discovery, PTFE played a pivotal role in the enrichment of Uranium-235 for the Manhattan Project due to its high chemical and thermal stabilities, specifically the ability to withstand hot uranium hexafluoride where every other gasket material failed. Since that time, PTFE has been used in a wide variety of applications where other materials do not possess the required properties, such as semiconductor manufacturing, chemical production, and aeronautics.[1] With global revenue for fluorochemicals topping $12.7 billion in 2008 and expected to increase at a rate of 2.6% per year, this area represents a large business.[2]

A wide variety of partially fluorinated and perfluorinated polymers can be prepared by copolymerizing different co-monomers with TFE. Addition of only a few mole percent hexafluoropropylene (HFP) produces the polymer referred to as fluorinated ethylene propylene (FEP).[3] While FEP does not have as high of thermal and chemical stabilities as PTFE, it has the added advantage of being melt-processable. Flow rates of PTFE at high temperatures are so low that it is considered impractical to produce products by blow molding or other traditionally used polymer fabrication techniques. Instead products made of PTFE are often processed by simply machining the product out of a large block of the virgin polymer. This wasteful and expensive method of processing resin leads to higher prices for the finished product. For many applications a material with slightly lower chemical resistance is adequate, and thus less expensive FEP has found use in the chemical industry. Other similar polymers are available by adding different co-monomers such as perfluoromethyl vinyl ether to give perfluoroalkoxy resin (PFA) or ethylene to give ethylene tetrafluoroethylene (ETFE).[3]

While the fluoropolymers previously mentioned are typically known for their inertness, perfluorinated ionomers are an interesting class of materials containing both an inert fluorocarbon backbone and a superacidic functional group. The most well-known and studied perfluorinated ionomer available is DuPont's Nafion®, discovered in the 1960s by Walther Grot. Nafion® found its first commercial use as a fuel cell membrane in the short lived Gemini space program, but later found demand in Japan's chlor-alkali industry during the phase out of mercury cells due to environmental and health concerns.[4] The use of a cell separated by a semi-permeable Nafion® membrane, which allows sodium cations to transport across but not chloride anions, proved to be a success and is widely used by this industry.[5] In 2010 the United States produced 10.5 megatonnes (10.5 million metric tonnes) of chlorine, approximately one quarter of that employs a chlor-alkali cell with a perfluorinated semi-permeable membrane.[5-6] Recently, with the rising costs and depleting reserves of fossil fuels, research is focusing on a similar technology, polymer electrolyte membrane fuel cells, to replace combustion powered vehicles.

The importance of TFE is not limited to its role as a monomer, but also includes its use as a building block for many other fluorocarbons. Reaction with iodine pentafluoride in the presence of an antimony pentafluoride catalyst yields pentafluoro iodoethane, which can be further reacted with TFE to yield longer chain perfluoro telomer iodides. One commercial application for telomer iodides involves reaction with ethylene and then textile products to yield water and oil resistant fabrics. Alternatively, telomer iodides can be reacted with hydroxide ions to yield the acid fluoride, which can subsequently be converted to a carboxylic acid for use as an emulsifier in the preparation of fluoropolymers.[7] Along with anhydrous hydrogen fluoride, hydrofluorocarbons, and metal fluorides, TFE is one of the major commodity chemicals in the fluorochemical industry having found uses in many different areas.

While polymers prepared from TFE have proven to be valuable products, academic research in this area has remained low due to safety concerns. Deflagrations of TFE into carbon black and tetrafluoromethane have been shown to have an exothermicity around 65 kcal/mol.[8] The kinetic barrier to deflagration can be overcome by both spot heating from the auto-polymerization of TFE and adiabatic expansion if the gas is quickly opened from high pressure to low pressure.[9] Additionally, reaction of TFE with oxygen is capable of forming polyperfluoroperoxides that are explosive and capable of deflagrating any remaining TFE.[9] Several industrial accidents with TFE have occurred, the first being in Arlington, New Jersey during the Manhattan Project that resulted in the destruction of the facility. More recently, several deaths have occurred at a PTFE plant owned by Daikan in Decatur, Alabama from the result of liquid TFE being exposed to air.[8b]

Industrially, TFE is produced by the pyrolysis of chlorodifluoromethane (R22) that is itself prepared by the partial fluorination of chloroform using hydrogen fluoride and an antimony pentafluoride catalyst.[10] The pyrolysis is typically carried out at temperatures above 650 ˚C under vacuum to produce predominately TFE through the difluorocarbene intermediate with hydrogen chloride as a byproduct.[10] Higher pressures and temperatures can be used to also generate hexafluoropropylene if desired. Continuous gas phase processes are typically setup for this reaction such that R22 is continuously flowed through a hot reactor bed, generating a constant supply of TFE with purities of 99.99999%, an important property for use in the semiconductor industry which requires high purities.

Academically it is not practical to setup a continuous flow-through system of R22 for the small quantities required. Three main routes to produce TFE in smaller quantities have been found. First, the pyrolysis of PTFE will yield TFE as the major component if performed under vacuum at temperatures of 600 - 700 ˚C to avoid HFP formation.[11] A major concern with this route is the possibility to produce perfluoroisobutylene (PFIB), a highly toxic compound,[12] at higher temperatures of 850 - 900 ˚C.[11] The second route, debromination of 1,2-dibromotetrafluoroethane ($495 per 100 grams) with activated zinc, requires expensive starting materials.[13] Finally, pyrolysis of pentafluoropropionate salts will yield an equimolar mixture of TFE, CO_2, and the corresponding metal fluoride in high yields.[14] U.S. Patent 5,345,013 assigned to the DuPont Company shows that TFE in the presence of at least 30 mol% CO_2 cannot deflagrate, showing the third route is not only the cheapest and easiest, but safest.[9]

1.2 Experimental

The preparation of TFE using pentafluoropropionate salts is not novel and the author received significant insight from previously reported articles on the subject as well as unpublished results from Professor Andreas Kornath and Dr. Alex Kaufmann.[10c] The preparation of TFE using this method is included for completeness as well as better documentation.

1.2.1 Synthesis and Drying of Potassium Pentafluoropropionate

To four 500-mL polyethylene bottles is added 450 mL of H_2O followed by slow addition of 400 g of KOH, supplied by Fischer Scientific. After cooling to room temperature, the solutions are added to a two-necked, 5-L round-bottomed flask with stir bar, and the solution is then cooled in an ice bath. A pressure-equalizing addition funnel with 3.0 kg of pentafluoropropionic acid (PFPA), supplied by SynQuest Labs, is attached to one neck of the flask and a water condenser to the other, at which point the PFPA is slowly added to the KOH solution. After complete addition of PFPA, the acidity of the solution is checked and if needed additional PFPA is added until the solution is slightly acidic. Bulk water is removed by vacuum distillation, while smaller samples of approximately 300 g of the salt are dried to completeness in a 1-L, heavy-walled, long-necked, round-bottomed flask at 160 ˚C and 50 mtorr dynamic vacuum overnight, prior to pyrolysis.

1.2.2 Synthesis and Drying of Sodium and Calcium Pentafluoropropionate

The sodium and calcium salts of PFPA were prepared on smaller scales than potassium pentafluoropropionate in much the same way. Equimolar mixtures of sodium or calcium hydroxide and PFPA are reacted, and after removal of bulk water, the resulting salts are dried at 160 ˚C and 50 mtorr dynamic vacuum overnight.

1.2.3 Pyrolysis of Potassium Pentafluoropropionate

Two 1-L, heavy-walled, long-necked, round-bottomed flasks filled with approximately 200 g of potassium pentafluoropropionate, are connected using a glass cross with an attached pressure gauge. The fourth attachment point of the cross is connected to a 3.79-L stainless steel cylinder converted into a trap. This stainless steel trap is evacuated on a vacuum line and cooled in liquid nitrogen. The flasks are slowly heated to 350 ˚C behind a blast shield, collecting the volatile products in the trap under dynamic vacuum. Over the course of the pyrolysis, a coating of frozen TFE and CO_2 builds up on the inside of the stainless steel cylinder, causing some clogging and poor heat transfer between the gases inside the cylinder and liquid nitrogen outside the cylinder. These issues lead to a slow pressure buildup despite the reaction being performed under dynamic vacuum. After the pyrolysis is complete or the pressure inside the system is above 500 torr, the stainless steel trap is allowed to warm inside a barricade away from personnel until it has sat for 1 day at room temperature to ensure the cylinder does not detonate upon further warming. Pyrolysis of 196 g of potassium pentafluoropropionate yielded 132 g of TFE and CO_2 in 94.8% yield. IR analysis of the gaseous mixture at 45 torr using a gas IR cell with a 20 cm length shows a spectrum which matches up well with literature reports. ^{19}F NMR analysis of the gas mixture bubbled through deuterated chloroform shows the material to be approximately 98% pure with no HFP or PFIB detected.

1.2.4 Accelerating Rate Calorimetry of Pentafluoropropionate Salts

To three different stainless steel bombs, with an approximate volume of 9 mL, is added 0.2815 g of sodium pentafluoropropionate, 1.2598 g of calcium pentafluoropropionate, and 1.5136 g of potassium pentafluoropropionate that is then dried on the accelerating rate calorimeter (ARC) at 160 ˚C and 80 mtorr overnight after handling in air. A heat-wait-search is performed on the salts using a heating step of 10 ˚C, heating rate of 10 ˚C/min, wait time of 15 minutes, and a final temperature of 400 ˚C.

1.2.5 Equipment for TFE Polymerization System

The following equipment was used in the design and construction of the TFE polymerization system seen in Figure 1.1:

Quarter inch (1/4”) stainless steel tubing: Swagelok product number - SS-T4-S-035-20

Fail-closed air-actuated valves: Swagelok product number – SS-4BK-5C

Ball valves for supplying air to air-actuated valve: Swagelok product number B-42XS4

Air-actuated valves to vacuum line: Whitley Company model number - 133SR

Pressure transducers: Ashcroft type G2 product number - A1906EP10

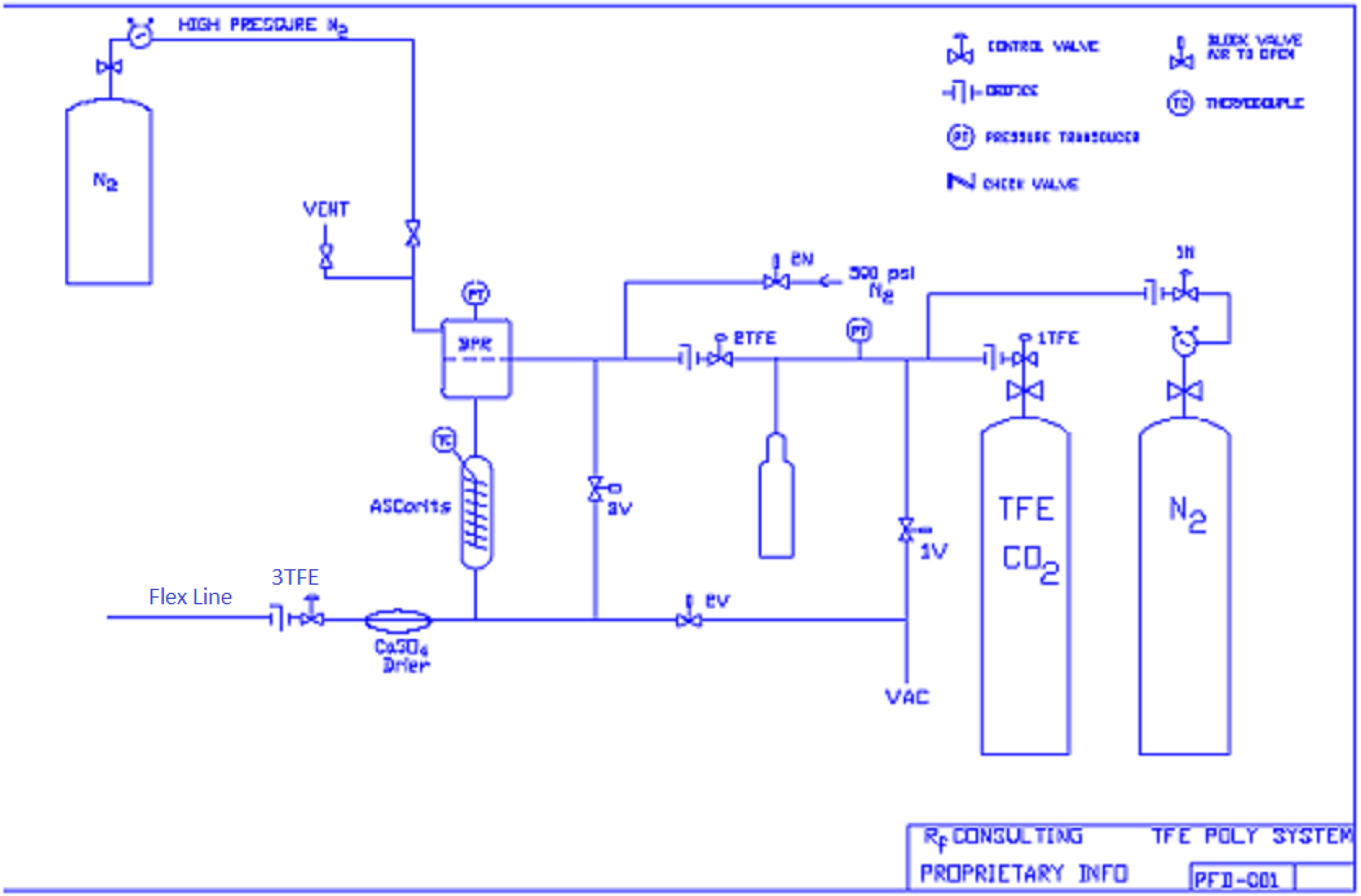

Figure 1.1. TFE polymerization system.

Back pressure regulator (Hastelloy C): Temco (Core Laboratories) product number BP-50-HC

Bellows-type, needle valves to control back pressure regulator: Swagelok product number - SS-4BMG

High-pressure, high-precision, syringe pump for initiator feed: Teledyne Isco® Model 100DM

Initiator line chiller: Thermo Fisher Scientific Digital One. Product number - R404A

Heater for 600-mL autoclave: Thermo Scientific. Product number - C40P

Heater for 100-mL autoclave: Parr Instruments 4836 controller

Six-point thermocouple readout: Honeywell eZtrend V5

Five-stage thermocouple readout: Omega Digicator

Four pressure transducer and tachometer readouts: Parr Instruments. Product number - A1960E

Hoke sampling cylinder - 316 stainless steel, 75 mL, spun cylinder

Stainless steel cylinder for carbon dioxide scrubber with stainless steel condenser jacket welded on the outside: Hoke sampling cylinder 4HD500 plus modification by UA, College of Arts and Sciences Machine Shop

Stainless steel cylinder for calcium sulfate drying column: Hoke sampling cylinder 4HD300

Stirred Parr® autoclaves - 100 and 600 mL stainless steel autoclaves with accompanying heating elements and Swagelok® fittings

1.2.6 Accelerating Rate Calorimetry Studies of CO_2 Absorbents

Two stainless-steel bombs are filled completely with Ascarite® and soda lime, placed on the instrument and evacuated. Each bomb is quickly opened and closed to a cylinder of dry CO_2 and monitored for pressure and temperature changes to determine the rate and exothermicity of CO_2 absorption for each material.

1.2.7 System Volume Measurements

To determine the volumes of the different portions of the polymerization system, the volume of a stainless steel cylinder is pre-determined to be 294 mL by mass balance after filling with water. This cylinder is attached to the system similarly as to how the TFE cylinder is attached. The system is equipped with both filled CO_2 (Ascarite) and water ($CaSO_4$) scrubbers, and the cylinder is pressurized with nitrogen to 101 psi before closing the air-actuated valve and venting the pressure from the rest of the system. With all valves closed and the BPR at 200 psi, TFE 1 is opened and the pressure on the system increases from 4 psi to 69 psi. After opening TFE 2 to allow the gas to flow to the BPR the pressure drops to 63 psi. Removing all pressure on the BPR and allowing the gas to flow to the manual valve on the flex tubing decreases the pressure to 28 psi. This measurement is performed three more times with different initial pressures, allowing the volumes of the system between TFE 1 and TFE 2, TFE 2 and the BPR, and the BPR and manual valve to be determined (by use of Boyles Law) at 440 mL, 50 mL, and 650 mL, respectively.

1.2.8 Ascarite II® Safety Tests on Polymerization System

To the CO_2 scrubber is added 8-20 mesh Ascarite II®, purchased from Acros Organics, using a plastic funnel screwed into the threads of the scrubber. Based upon the ARC studies of Ascarite® showing the material performs better when slightly wet, the Ascarite® is quickly added in the open atmosphere to absorb some moisture from the air. Addition of the 6-point thermocouple is done by gently shaking the scrubber as the thermocouple is inserted. After attaching the scrubber to the system and leak checking, dry CO_2 without TFE was pressurized up to the BPR. The pressure between TFE 1 and the BPR is then lowered by 12, 24, 48, and 96 psi by reducing the BPR dome pressure. The maximum temperature reached on each pen of the six point thermocouple is recorded. Based on the volume of the system, pressure change, and assuming an equimolar mixture of TFE and CO_2, it was determined that the amount of CO_2 added in each case was similar to adding 1.3, 2.5, 5.0, and 9.8 g of TFE from the mixture.

1.2.9 Standard Operating Procedure for TFE Polymerizations

- The system begins with all pneumatic and manual valves closed. If CO_2 scrubbing will be performed, the CO_2 and water scrubbers are filled with Ascarite II® and Drierite®, respectively, and attached to the system and water cooling using the jacket around the scrubber is started. Otherwise tubing that bypasses these scrubbers is added.
- All co-monomers, solvents, and salts are added to the autoclave inside a glove box with oxygen and water contents each below 5.0 ppm. The autoclave is sealed inside the glove box, removed from the glove box using the antechamber, and then placed in a tabletop vice allowing the bolts to be further tightened with a wrench.
- The autoclave is attached to the flex tubing on the system with the manual valve still closed and the autoclave heater is started. All other connections are attached including the thermocouple probe, pressure gauge, stirring mechanism with attached tachometer, and initiator line. For solution polymerizations, the initiator chiller is turned on to -10 ˚C to prevent the initiator from decomposing before entering the autoclave.
- Valves Vacuum 1, TFE 2, TFE 3, and the flex tubing valve are opened in that order to evacuate air out of the system.
- Valve Vacuum 1 is closed and valve Nitrogen 2 is opened. The system is pressurized to at least 100 psi above the maximum expected operating pressure for the polymerization. All connections on the system, especially any new connections, are leak checked using Snoop® and retightened if any leaks are found.

- Valve Vacuum 2 is opened and the system is evacuated. Afterwards, the manual valve on the autoclave is quickly opened and closed several times to remove nitrogen from the autoclave. The valve is quickly opened and closed to prevent loss of monomer or solvent and then the manual valve is closed.
- The system is filled with nitrogen to 100 psi and evacuated two more times and left under vacuum.
- The initiator storage container is stored under dry ice to prevent the initiator from decomposing and kept under a nitrogen pad to keep air out. Using the ISCO® pump a quantity of 10 mL of initiator is added by pressing the refill button. Both valves on the ISCO® pump are closed and the run button is pressed until the pressure reading of the pump reads above 200 psi, at which point the stop button is pressed. The ISCO® pump valve leading to the autoclave is opened and the 3-way valve at the end of the initiator line is turned to vent the pressure to an Erlenmeyer flask. The run button is pressed on the ISCO® pump until the piston is empty, at which point the 3-way valve and pump valves are closed. This process is repeated one more time and then sufficient initiator for the polymerization is filled into the pump. The Erlenmeyer flask with the initiator solution is sealed with a rubber stopper for several days at room temperature to allow all 3P to decompose to CO_2 and likely perfluorobutane.
- The initiator line is pressurized up to the closed 3-way valve and the pressure is vented before closing the ISCO® pump valve and opening the 3-way valve on the initiator line to the autoclave. All manual valves on the system including the autoclave, flex tubing, and TFE/CO_2 storage cylinder are opened before the polymerization bunker door is closed and the room remains off limits to personnel for the remainder of the polymerization.

- With all pneumatic valves closed, valve TFE 1 is opened pressurizing the first portion of the system to the desired pressure, then closed.
- The BPR dome is pressurized to 100 psi above the reading on pressure gauge TFE 1. Valve TFE 2 is opened allowing the TFE/CO_2 mixture to flow up to the BPR.
- The BPR dome pressure is slowly lowered until TFE and CO_2 start flowing into the second portion of the system. If the CO_2 scrubber is installed valve TFE 3 is left closed during the additions while the temperature on the six-point thermocouple is monitored and the additions of TFE/CO_2 are halted if the temperature begins approaching 50 ˚C. After 20 psi of neat TFE is present on the second half of the system and the six-point thermocouple is near room temperature, valve TFE 3 is opened and the autoclave is filled to the operating pressure. If the CO_2 scrubber is not installed, valve TFE 3 can be opened as soon as the BPR dome pressure is lowered.
- Once the system is at the operating temperature and pressure, the run button on the ISCO® pump is pressed until the pressure in the pump is the same as the pressure in the autoclave. Once the flow rate is set to the desired amount, the manual valve on the ISCO® pump is opened to the initiator line and the run button is pressed, adding initiator and starting the polymerization. If at any time the flow rate needs to be changed, it can be done so using the ISCO® pump control panel without stopping the polymerization.
- The polymerization is allowed to continue for the desired amount of time, adding more TFE as necessary. Once the polymerization is complete, the ISCO® pump is stopped and the manual valve closed while the polymerization is allowed to sit overnight.
- After sitting overnight, all pneumatic valves are closed on the system from the control panel. The operator enters the room and closes all manual valves on the system,

specifically the autoclave and flex tubing valves before removing the autoclave from the system and taking it to a fume hood. Excess TFE/CO_2 pressure is vented into the hood before disassembling the autoclave and commencing workup.

1.3 Results and Discussion

1.3.1 Tetrafluoroethylene Synthesis and Studies

Based upon the ease of reaction, low cost of starting materials ($399 per kg PFPA and minimal cost for KOH) and safety aspect of having 50 mol% CO_2 present, it was decided to use the pentafluoropropionate route for production of TFE in our laboratory. Accelerating rate calorimetry (ARC) studies were performed on the decomposition of sodium, potassium, and calcium pentafluoropropionate salts. Sodium pentafluoropropionate, shown in Figure 1.2, begins decomposing slowly at 230 ˚C and does not finish for roughly 100 minutes, even as the temperature is slowly increased to 260 ˚C. Potassium pentafluoropropionate, shown in Figure 1.3, begins decomposing rapidly at 290 ˚C and is finished within minutes. Whereas the decompositions of the potassium and sodium salts are both endothermic, it was hypothesized that the strong lattice energy of calcium fluoride at -2,609 kJ/mol, compared to -910 kJ/mol for sodium fluoride and -808 kJ/mol for potassium fluoride, might cause its decomposition to be less endothermic or possibly even exothermic, increasing yield and decreasing reaction time, but also possibly causing safety concerns when done on a larger scale depending on the exothermicity of the reaction. As shown in Figure 1.4, at 280 ˚C, the calcium salt begins decomposing, and the ARC shows a slight exotherm. However, despite drying the calcium salt at 160 ˚C and 80 mtorr (similar procedure to that used for the potassium and sodium salts), it appears water is still present as a hydrate due to a small pressure increase and large endotherm seen at 160 ˚C during the heat-wait-search. It also appears that the calcium salt is not completely reacted at 280 ˚C and

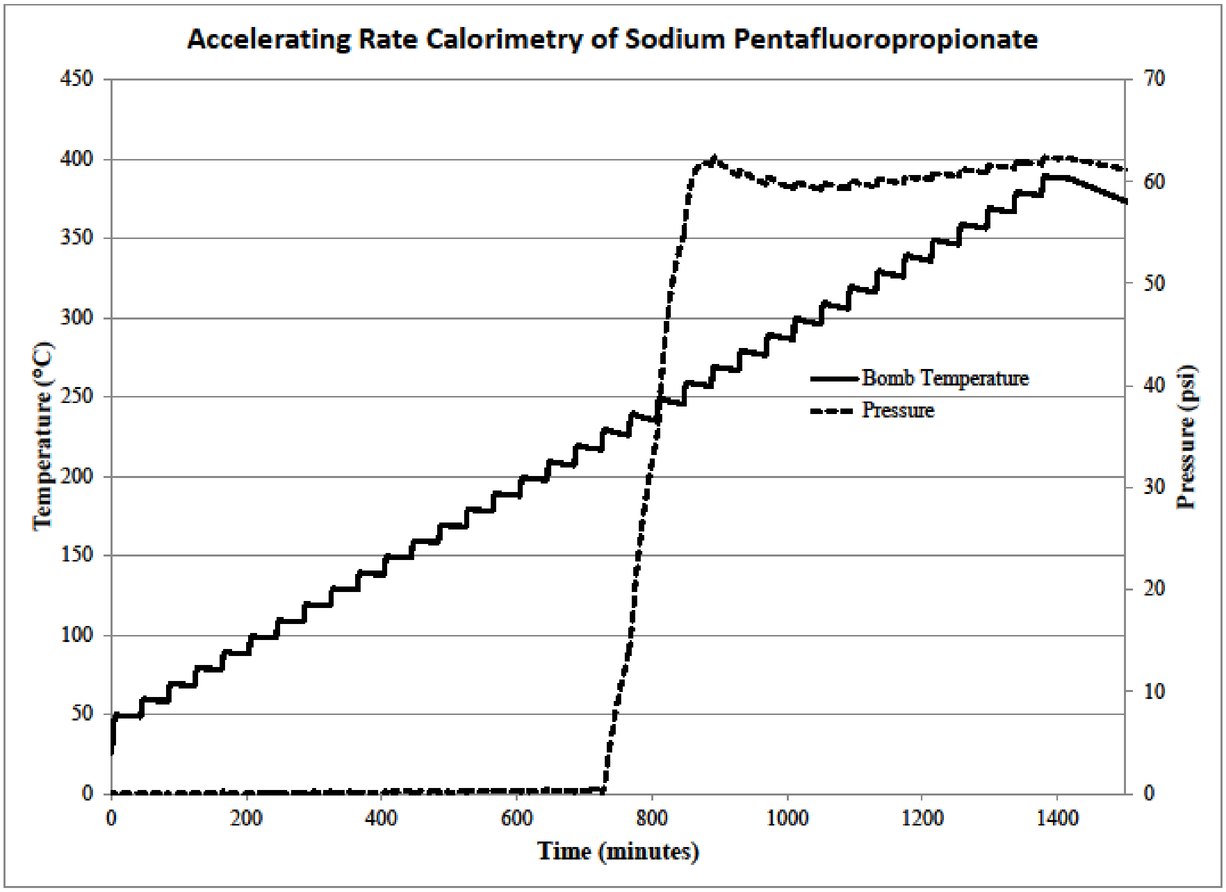

Figure 1.2. Accelerating rate calorimetry data from sodium pentafluoropropionate

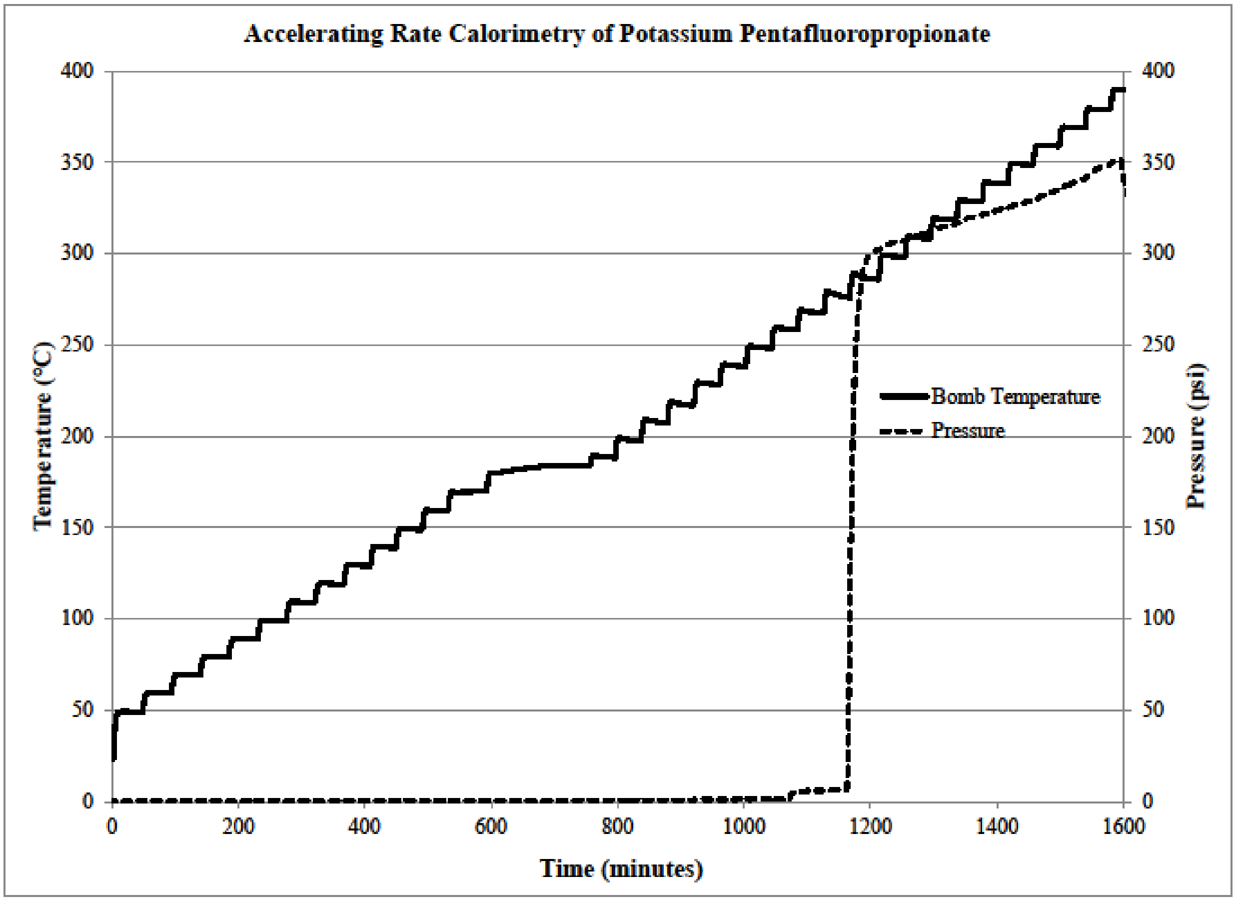

Figure 1.3. Accelerating rate calorimetry data from potassium pentafluoropropionate

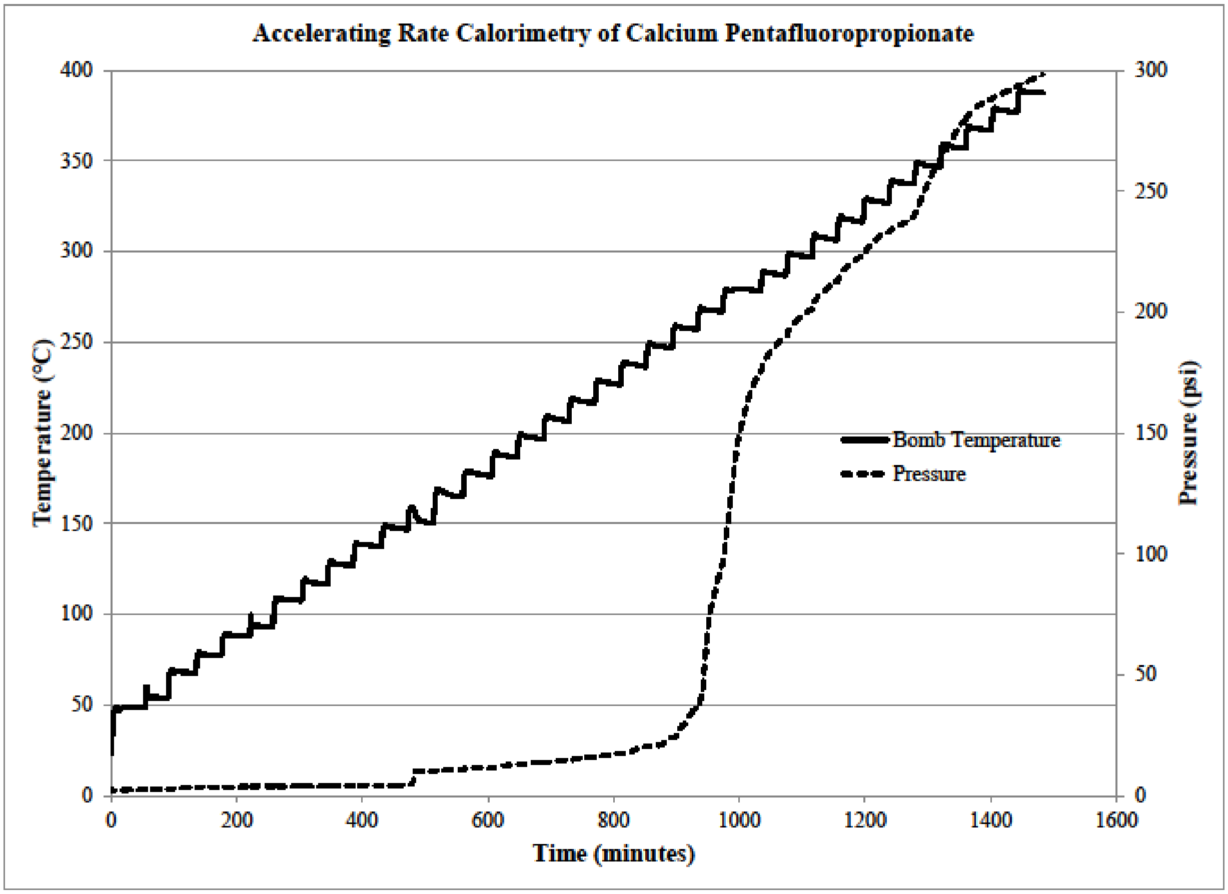

Figure 1.4. Accelerating rate calorimetry data from calcium pentafluoropropionate

keeps slowly decomposing even up to 350 ˚C. The difficulty in completely drying the calcium salt that would be exacerbated on a larger scale and at the higher temperature required to obtain complete reaction would lower yields, and thus the calcium salt was not explored on a larger reaction scale.

During pyrolysis of the sodium and potassium salts, it has been observed that the sodium salt melts before the decomposition point while the potassium salt decomposes before melting. Since the hottest area of the salt during pyrolysis is in contact with the flask, decomposition of the molten salt under vacuum leads to severe frothing up the neck of the flask. This was believed to pose a safety hazard, and thus potassium pentafluoropropionate has been selected as the salt of choice for producing TFE. By collecting all volatile products from the reaction into a trap cooled to -196 ˚C under dynamic vacuum, an equimolar mixture of TFE and CO_2 can be produced and stored safely without the needed addition of an inhibitor such as limonene. As can be seen in the ARC measurements performed here, TFE does not deflagrate at temperatures up to 400 ˚C and a pressure of 350 psig in agreement with the more rigorous testing done by the DuPont Company highlighted in U.S. Patent 5,345,013.[9]

Drying of the potassium pentafluoropropionate salt must be done under vacuum as it has been observed that the material melts when the wet salt is heated to 160 ˚C at atmospheric pressure. Alternatively, when dried under a vacuum of less than 100 mtorr, the salt does not melt before its decomposition at 280-290 ˚C. Two samples of potassium pentafluoropropionate, 311.35 g and 348.96 g, which had been heated to 160 ˚C at atmospheric pressure were further dried under vacuum at 160 ˚C yielding 302.75 g and 342.69 g of dried salt, respectively. Mass balance after water loss suggests that unless dried under vacuum the salt crystallizes as $CF_3CF_2CO_2K \cdot \frac{1}{3}H_2O$. As the decomposition of the pentafluoropropionate produces a carbanion that will abstract a proton from any trace water to yield pentafluoroethane, the material must be scrupulously dried under vacuum before pyrolysis to give high yields of TFE.

Analysis of the purity of the TFE and CO_2 mixture was performed by both IR and NMR spectroscopy. The most likely contaminant would be pentafluoroethane, HFC-125, which is produced from traces of water present during the pyrolysis. In the IR spectrum, no C-H stretch can be seen at 3000 cm^{-1} or the more characteristic stretch seen at 1208 cm^{-1} as reported in literature for HFC-125. The recorded spectrum, shown in Figure 1.5, matches well with those reported in the literature with the added stretch attributed to CO_2. Small quantities of the product were bubbled into an NMR tube containing chloroform-d spiked with $CFCl_3$, with the ^{19}F NMR spectrum showing a singlet at -132 ppm attributable to TFE as seen in Figure 1.6. The presence of less than 1% of a pentafluoroethane impurity can be detected by ^{19}F NMR spectroscopy.

1.3.2 Tetrafluoroethylene Polymerization System

Design of the TFE polymerization system keeps safety of personnel as the primary focus due to the deflagration hazard posed by TFE. Multiple levels of safety have been employed; each designed to prevent the subsequent levels from being used. The use of TFE with 50 mol% CO_2 present prevents the chance for deflagration and polymerizations were always attempted with CO_2 present unless circumstances required its removal. For these circumstances, additional levels of security were employed to prevent the neat TFE from deflagrating. First, the CO_2 scrubber is placed after a back pressure regulator (BPR), allowing the flow rate of the TFE/CO_2 mixture to be controlled such that the exothermic reaction between CO_2 and the absorbent does not reach unsafe temperatures. Secondly, a six point thermocouple is installed inside the water cooled scrubber such that the temperatures can be monitored and controlled. Finally, 0.010 inch orifices are added strategically throughout the system such that as valves are opened, high

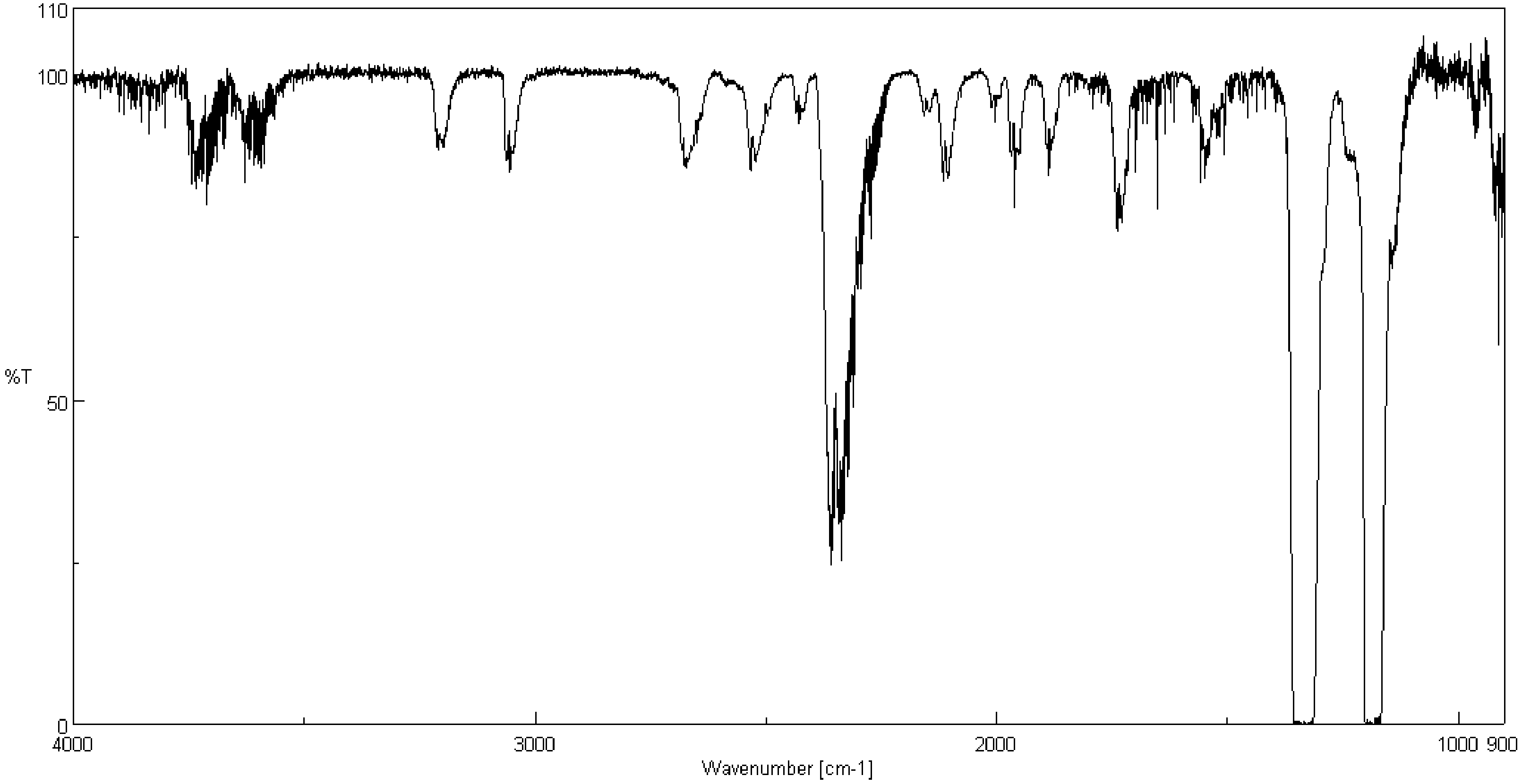

Figure 1.5. Infrared spectrum of TFE and CO_2 mixture at 45 torr.

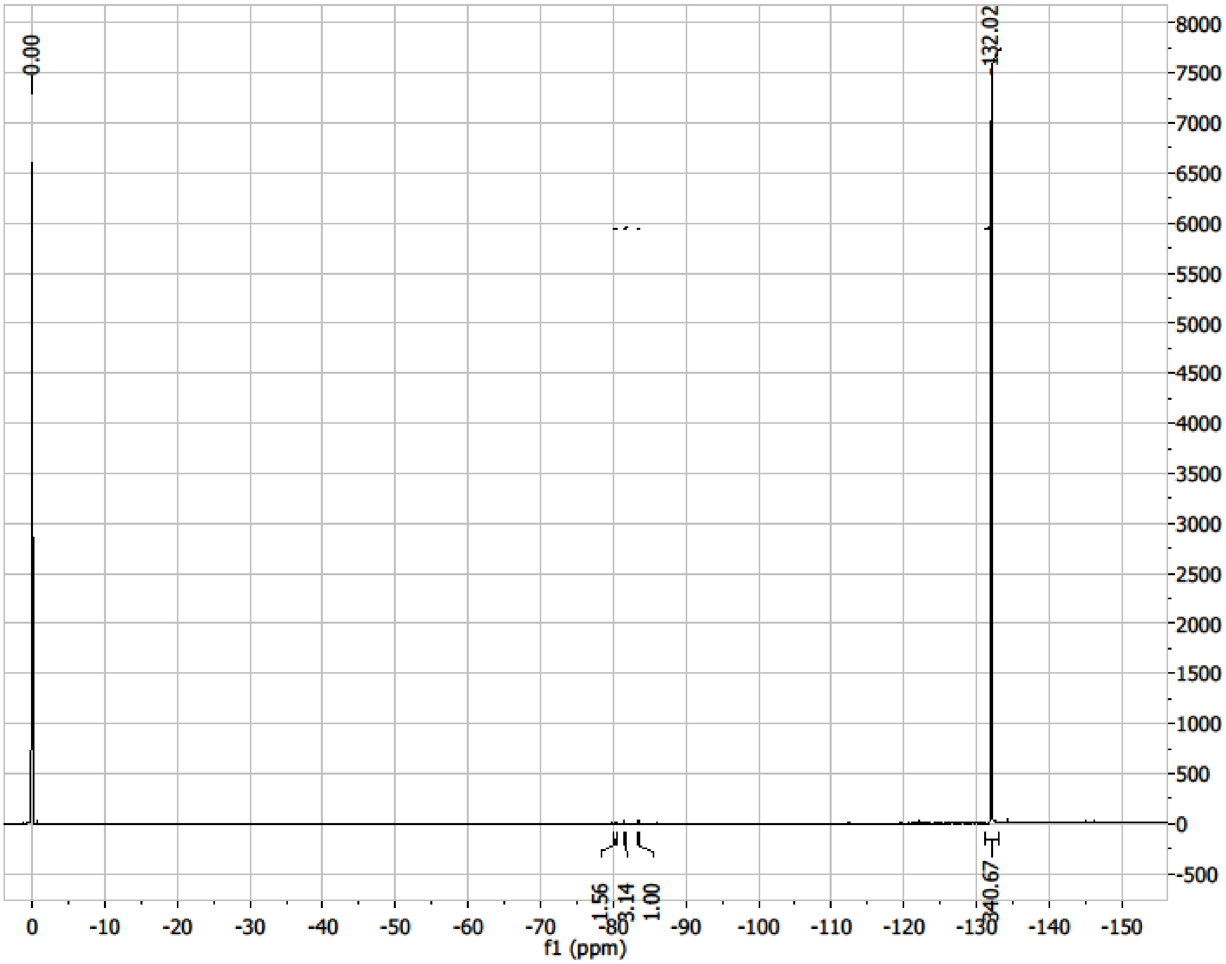

Figure 1.6. ^{19}F NMR spectrum of TFE and CO_2 bubbled into $CDCl_3$ containing traces of $CFCl_3$.

pressure TFE flows more slowly to the low pressure sides, reducing the chance of adiabatic expansion causing deflagration. As the highest pressures are located in the TFE storage cylinder, one orifice is placed after pneumatic valve TFE 1. Another orifice is placed on the BPR outlet to prevent TFE and CO_2 from flowing too quickly into the scrubber if operator failure leads to BPR pressure being lowered too quickly.

Verifying the effectiveness of absorbing CO_2 for both Ascarite II® (Ascarite) and soda lime was first tested on small scales using the ARC. For the soda lime filled bomb, the pressure began instantly dropping from 100 to 10 psi over 5 minutes, although at an exponentially decreasing rate, during which time the temperature of the system increased from 20 ˚C to 95 ˚C. Conversely, the pressure in the Ascarite bomb initially dropped at a low rate when 210 psi of CO_2 was added, only decreasing 10 psi over the first five minutes. However, as more water is produced from the reaction of NaOH and CO_2, transforming the reaction from solid-gas phase to a solution phase reaction, the rate of pressure drop increases significantly, showing a pressure decrease from 190 psi to 29 psi in just 41 seconds. Additionally, the temperature increased less than 40 ˚C despite scrubbing a larger quantity of CO_2 than in the soda lime trial. While the heat of reaction for carbon dioxide reacting with sodium hydroxide is higher than with soda lime, -287.91 kJ/mol compared to -221.51 kJ/mol, the temperature increase for the Ascarite reaction was lower than for soda lime despite a more rapid pressure decrease. Also, Ascarite does a better job removing all of the CO_2 as it takes less than 2 minutes to drop from 28 to 0 psig with Ascarite, while it takes over 7 minutes for the same pressure drop to occur with soda lime. Based upon Ascarite's increased rate of removing CO_2 as well as the lower temperature increases for the reaction, it was determined to use it over soda lime.

To determine the flow rates of TFE and CO_2 that can safely be added through the CO_2 scrubber on the system, neat CO_2 was added to the scrubber in quantities greater than would be needed. To further simulate a worst case scenario, the water chiller around the scrubber was not turned on. It was found that temperatures up to 100 ˚C were seen with the addition of 24 psi of neat CO_2, or 48 psi of the combined mixture corresponding to 2.5 g TFE (see Figure 1.7). With the thermocouples spaced two inches apart within the scrubber, it was observed that as the Ascarite becomes exhausted and the reactive area moves down the scrubber, the highest temperature in the bed may be between the pens in the thermocouple, resulting in the highest temperature in the column not being recorded. It was determined that no more than 20 psi of the mixture of TFE and CO_2 should be added at one time to prevent the scrubber from reaching temperatures above 50 ˚C.

A sample of the 1 : 1 mixture of TFE and CO_2 is slowly added to the Ascarite II® scrubber with the water coolant running with care taken to never let the six-point thermocouple record a temperature above 35 ˚C. To a gas IR cell is added 45 torr of the resulting and the FTIR spectrum is recorded (see Figure 1.8). This spectrum confirms the absence of an absorbance from CO_2 and the spectrum matches closely with literature reports for TFE.

While great lengths are taken to prevent deflagration no way exists to guarantee it will not occur while working with TFE, especially once CO_2 has been removed. Due to this concern, efforts were taken to minimize the operator’s exposure in the event of deflagration. The entire system is isolated within the Shelby Hall attic that requires special access to reach, and built inside a barricade with increased rebar support in the walls. Additionally, to vent any pressure buildup from a deflagration, parts of the ceiling are designed as weak spots to quickly dissipate pressure buildup. The TFE storage cylinder itself is located behind a half inch thick steel

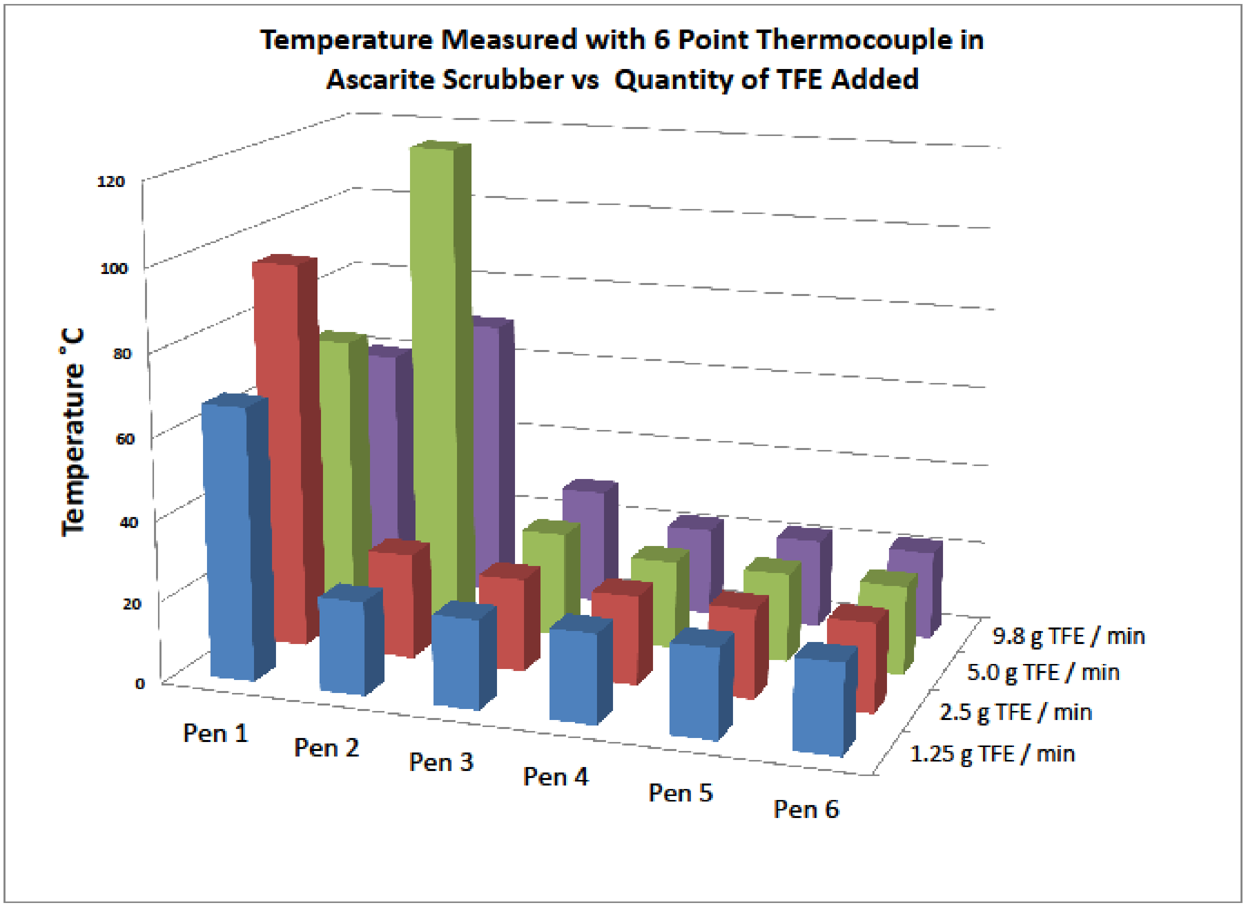

Figure 1.7. Maximum temperatures recorded after adding specific quantities of CO_2 to Ascarite® scrubber on system.

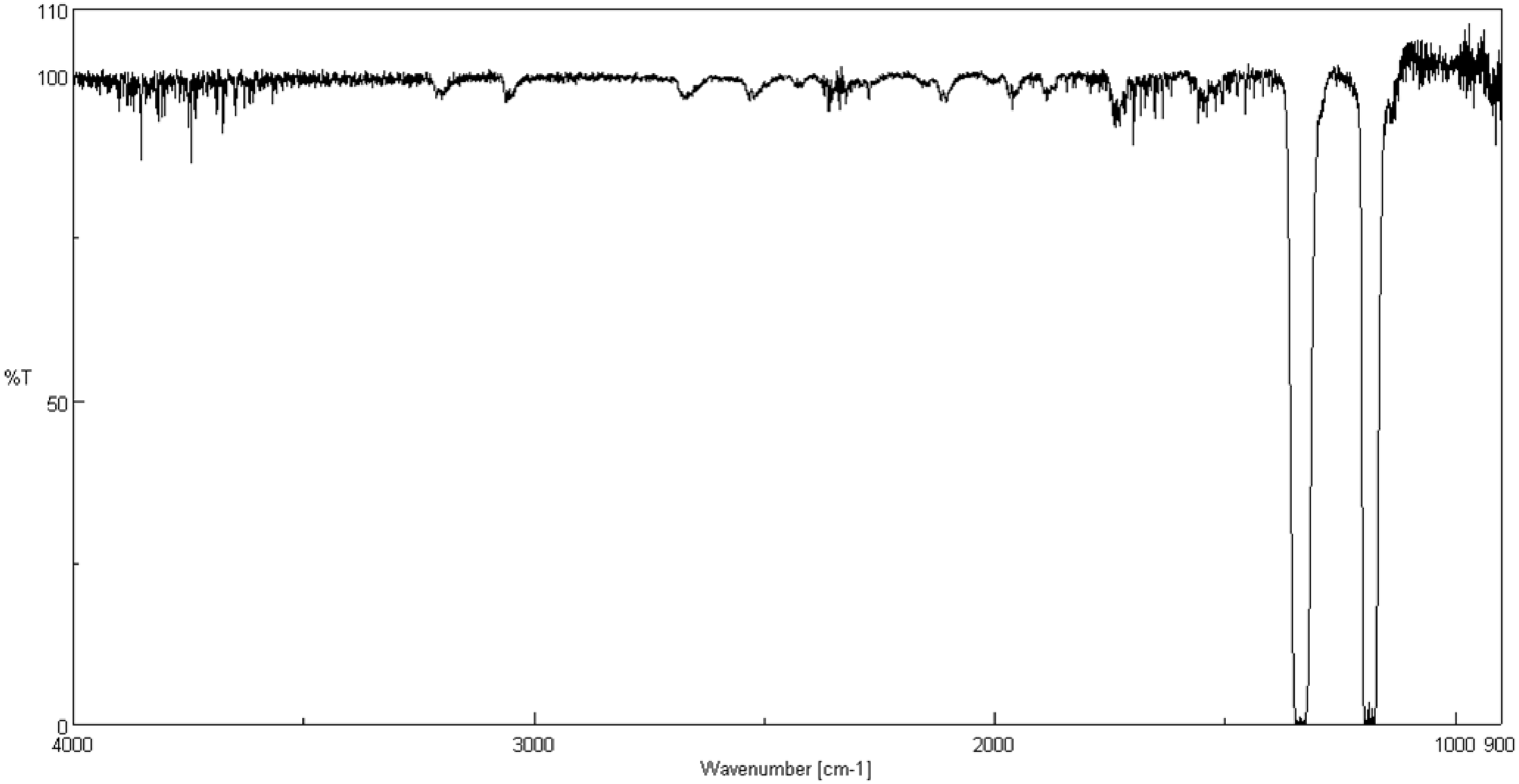

Figure 1.8. IR spectrum of gas after flowing mixture of TFE and CO2 through Ascarite® scrubber.

barricade to reduce the possibility of any flying shrapnel. Polymerizations can be remotely controlled from outside the barricade using fail-closed, air-actuated valves and needle-nose valves on the control panel. Air-actuated valves were chosen over electrical valves to reduce the risk of electrical sparks igniting the TFE. Also mounted on the control panel are digital temperature, pressure, and tachometer meter readouts from the system as well as a display for the 6-point thermocouple. Thus, the entire polymerization can be controlled and monitored from outside the barricade to minimize exposure of the operator in case of deflagration.

Other features of the system include an ISCO® pump located outside the polymerization room that allows specific volumes of initiator to be added to the autoclave. Flow rates can be input into the control panel of the pump by selecting the flow rate and manually inputting values using the number pad. The 1/16” outer diameter tubing from this pump is encased inside 3/8” outer diameter copper tube where coolant from a chiller flows between the two tubes, allowing the initiator to be kept cold until it reaches the autoclave. Two pneumatic valves, controlled from the control panel, allow the system to be opened to a vacuum line to easily remove oxygen and nitrogen from the system. Three different sizes of autoclave are available for the polymerizations, namely 50-mL, 100-mL, and 600-mL, each equipped with a magnetic drive stirrer, thermocouple, pressure transducer, and a dip tube for initiator additions. Through careful handling, no accidents or problems have arisen from the work with TFE, and none of the secondary safety precautions designed to minimize the damage from an explosion have ever been needed.

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CHAPTER 2

COPOLYMERS OF TETRAFLUOROETHYLENE AND PSEPVE/DOW

2.1 Introduction to Nafion® Polymers

Preparation of perfluoro-2-(2-fluorosulfonylethoxy) propyl vinyl ether (PSEPVE) is typically performed in industry using a flow process for the series of reactions shown in Figure 2.1. The process involves the reaction of tetrafluoroethylene (TFE) with sulfur trioxide at room temperature to yield the corresponding TFE sultone. This TFE sultone ring opens in the presence of fluoride ions to form the alkoxide, which is stabilized from rearranging to the acid fluoride by the electron withdrawing sulfonyl fluoride. Addition of the first equivalent of hexafluoropropylene oxide (HFPO) occurs selectively to form the mono-adduct; however, subsequent additions of HFPO are less selective. This lack of selectivity leads to the reaction's difficulty, namely in controlling the number of HFPO monomers added to predominately form the di-adduct in high conversion since stoichiometric amounts of HFPO yield a statistical distribution of the mono-adduct, di-adduct, and the higher orders. To overcome this issue on the industrial scale, a quite ingenious continuous process was devised in that only a small equivalent of HFPO is added to the reactor such that there always exists a high concentration of the mono-adduct and only small amounts of the product. After distillation, the di-adduct is isolated while the mono-adduct is sent back to the reactor pot for further reaction. Thermal rearrangement of this di-adduct in the presence of sodium carbonate forms PSEPVE, which must be distilled under vacuum as it rearranges to form an acid fluoride at its normal boiling point of 135 ˚C.[1] This setup prevents the loss of material to the higher adducts that have no chemical value. Despite the low costs of the starting materials, which are all common building blocks, the monomer still has a high value ($1,100 per kg price direct from the manufacturer) due to this difficult engineering.

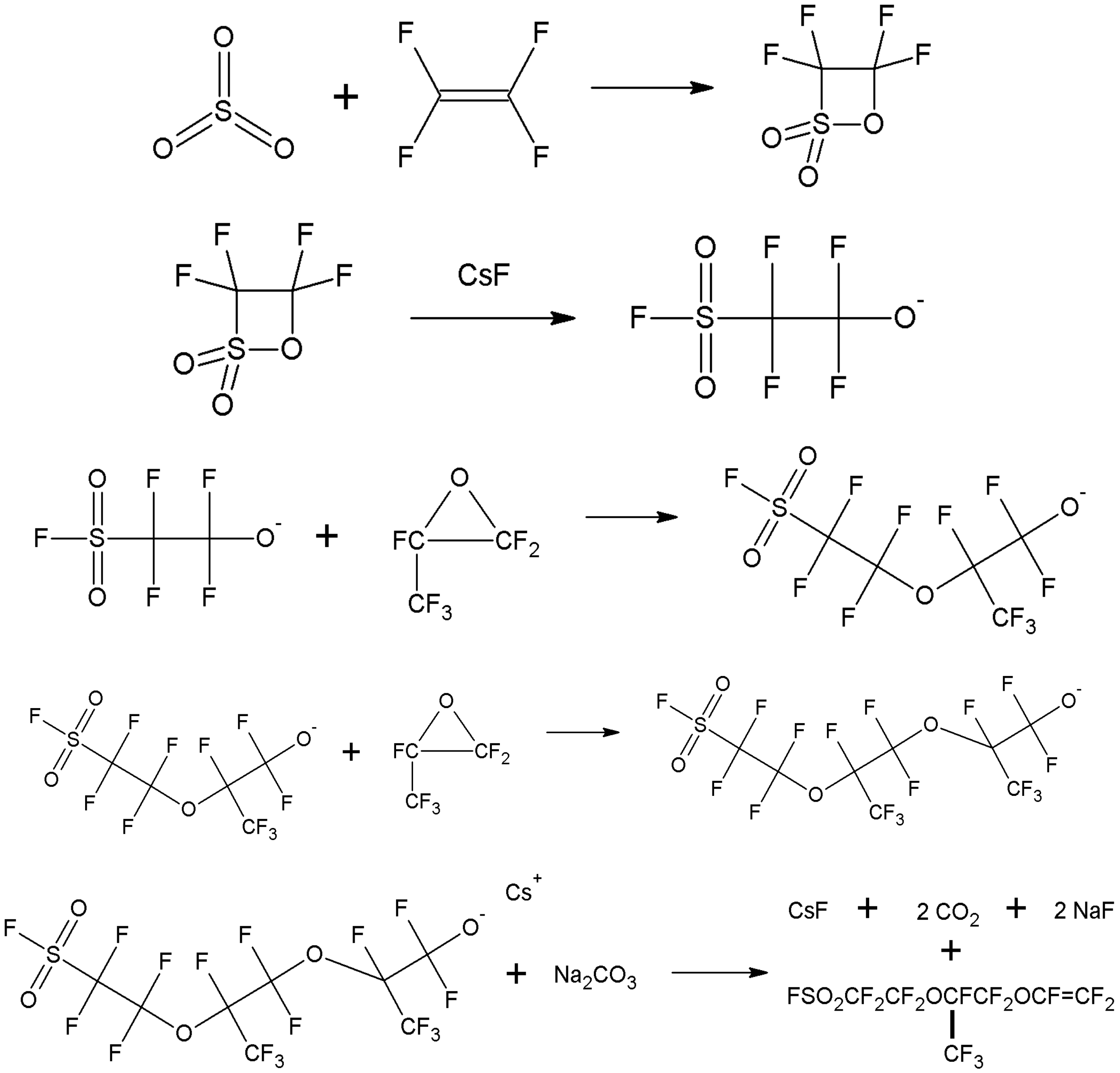

Figure 2.1. Industrial preparation of PSEPVE.[1]

Other similar perfluorinated vinyl ether sulfonyl fluoride monomers exist, such as perfluoro-3-oxa-4-pentene sulfonyl fluoride (Dow). This monomer was first synthesized by the Dow Chemical Company using a single equivalent of chloropentafluoropropylene oxide (CPFPO) in place of two equivalents of HFPO, followed by dehalogenation with zinc. More recently, Solvay Solexis company has discovered a new method to form this monomer, using elemental fluorine to ring open the TFE sultone, yielding a hypofluorite, which is reacted with 1,2-dichloro-1,2-difluoroethylene before dechlorination with zinc to form the monomer, as seen in Figure 2.2. Solvay Solexis's route has found more industrial use than Dow's method, allowing for the commercialization of this monomer.[1-2]

While both PSEPVE and Dow are prepared regularly on an industrial scale, their syntheses on the laboratory scale is uncommon. Literature reports exist for the preparation of PSEPVE in an academic lab, but overall yields are as low as 30%.[3] For the Dow monomer, low yields using the original CPFPO method as well as the hazards of working with large quantities of elemental fluorine and perfluorinated hypofluorites make it potentially dangerous to prepare in large quantities in an academic laboratory. Multi-step reactions that require purification after each step would also require far too much time investment simply to produce a commercially available, albeit expensive, reagent.

Copolymers of PSEPVE with TFE prepared by the DuPont Company are sold under the trade name Nafion®; however, both the Asahi Glass and Asahi Chemical Companies from Japan sell similar materials as well.[4] The materials are classified by their equivalent weight (EW), or grams of polymer required to neutralize 1 mole of base. Typically the polymers are sold post-hydrolysis and in membrane form or as dispersions in a water-propanol mixture. Nomenclature for the membranes combines the EW and the thickness of the membrane, such that N117

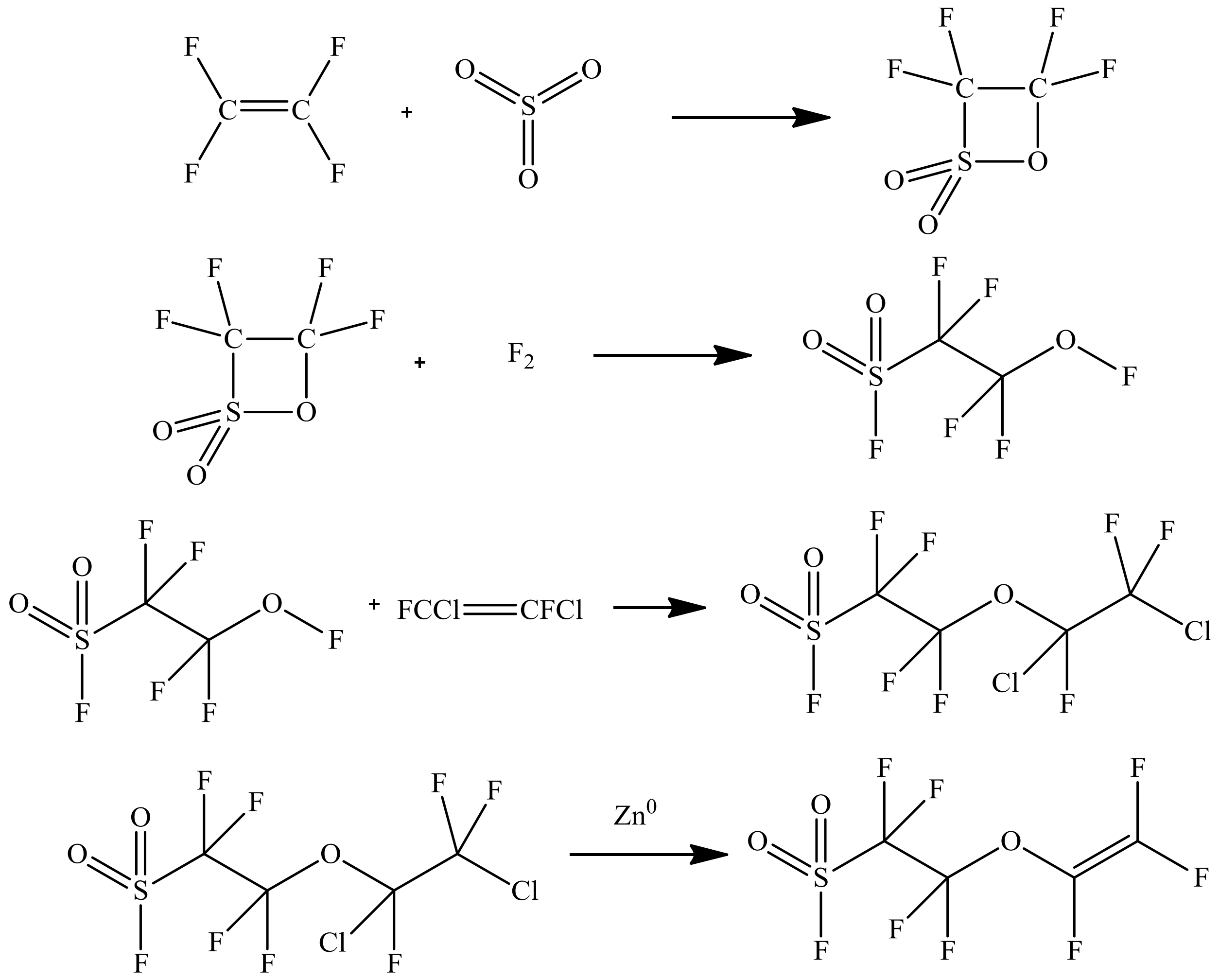

Figure 2.2. Industrial Preparation of Dow vinyl ether monomer.[1]

represents a Nafion® membrane with an EW of 1100 and thickness of 7 millinches (mils). The most common EWs sold are 1100 and 1000, which are designed to balance the conductivity and mechanical properties; however, some lower EW samples are also sold. The properties for these high EW samples are optimized primarily for use in chlor-alkali cells where large membranes are immersed in water during operation. In this application, mechanical strength is valued more at the expense of conductivity, unlike polymer electrolyte fuel cells that benefit from increased conductivity at the loss of mechanical strength.

Polymer electrolyte membrane fuel cells (PEMFCs) allow a fuel, such as hydrogen, to be electrochemically converted to useful energy as seen in Figure 2.3.[5] At the anode of the membrane electrode assembly (MEA), hydrogen is split into protons and electrons by platinum nanoparticles dispersed on a porous carbon support. A semi-permeable membrane allows the transport of protons across it to the cathode, while electrons can only reach the cathode by flowing through an external circuit, yielding usable electricity. At the cathode, oxygen from the air reacts with the protons and electrons to yield water as the only byproduct of the fuel cell, classifying fuel cells as a green technology, depending how the hydrogen is produced. Fuel cells hold promise in helping to reduce America's dependence on foreign oil as the hydrogen fuel can be produced from natural gas, coal, and water electrolysis, resources abundant in America.[6]

Despite the promise of fuel cells, several technological hurdles still exist that have prevented the commercialization and mass production of fuel cells, including the large amounts of platinum needed as a catalyst in the MEA,[7] the ability to produce,[6] transport, and store the hydrogen,[8] and membrane limitations.[9] While the platinum and hydrogen issues have a bigger impact on mass production much further in the future, the more immediate issue, which will be the focus of this dissertation, involves membrane limitations.

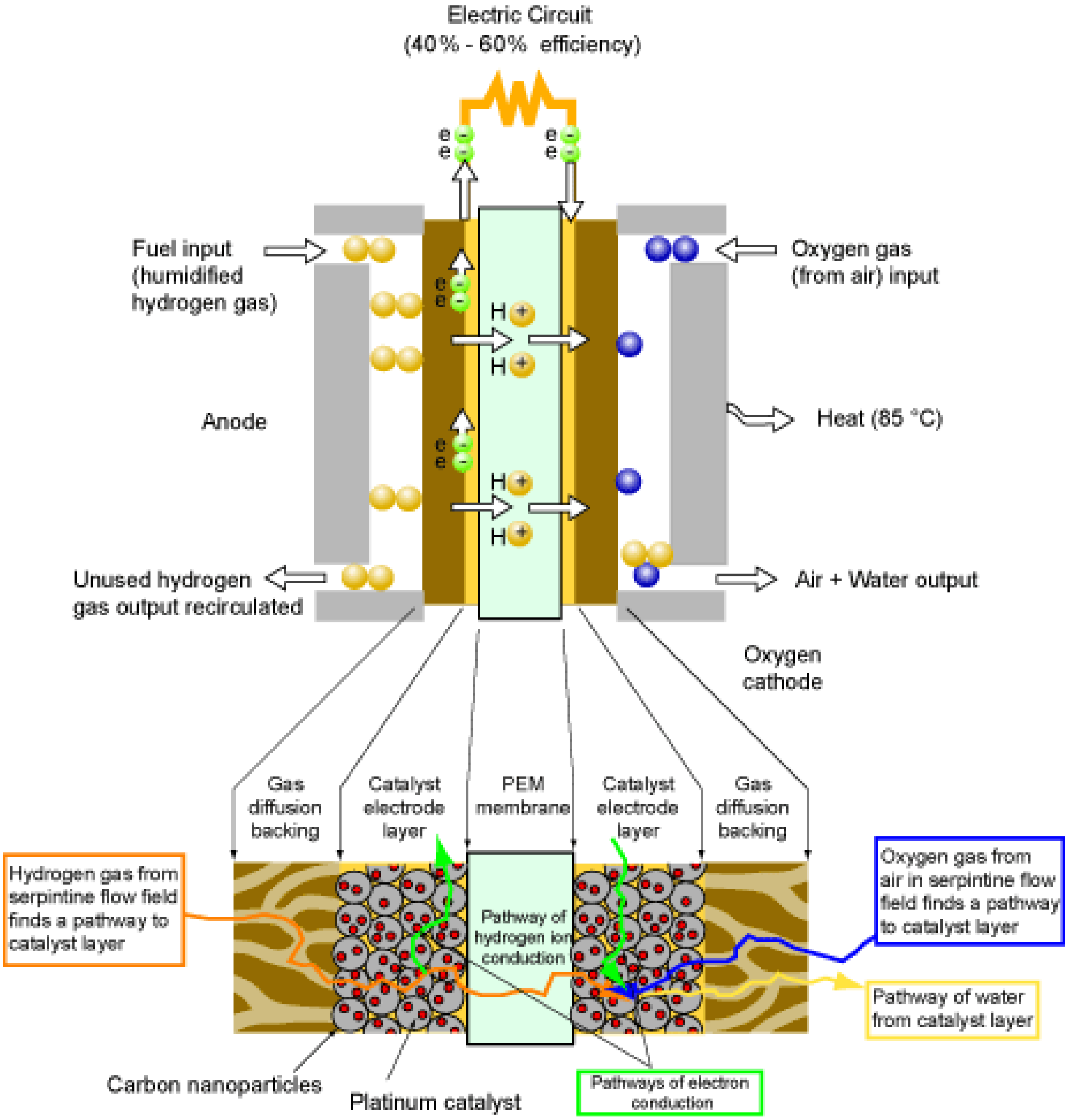

Figure 2.3. Fuel cell schematic. Reproduced with permission.[5]

Nafion® remains the standard for PEMFC membranes due to its thermal and chemical stabilities preventing degradation within the cell, its high dielectric strength reducing electronic current from passing through the membrane, and superacidic functional group giving high proton conductivity; however, several limitations still exist with Nafion® membranes.[10] The proton conductivity of Nafion® is directly related to the relative humidity (RH)[11] as evidenced by Figure 2.4. While this is not detrimental for the main commercial use of Nafion®, chlor-alkali cells where the membrane is immersed in water, it presents a major problem in fuel cells. This relation of conductivity to level of hydration is based on two different mechanisms of proton transport through the membrane, shown in Figure 2.5. Above approximately 20% relative humidity the vehicular mechanism, where unbound water molecules transport protons through the membrane by osmosis and gradient driven diffusion, is the dominant proton transport mechanism. Higher levels of hydration increase the amount of bulk water and allow for better proton transport using the vehicular mechanism. At hydration levels below 20% protons are transported by the hopping mechanism, where transport occurs between individual sulfonic acids on the side chains, a slow mechanism that severely limits conductivity.[10] Literature reports show the conductivity of Nafion® increases in a linear fashion as relative humidity is increased from 20% to 100%.[11-12] As the relative humidity drops below 20%, a more dramatic decrease in conductivity appears as hopping becomes the more dominant mode of proton transport. This dramatic drop-off in conductivity restricts usage of Nafion® to more humid operating conditions.

During operation, fuel cells produce a large amount of heat that in vehicles must be removed by the radiator. Vehicle size specifications limit the size of the radiator and its ability

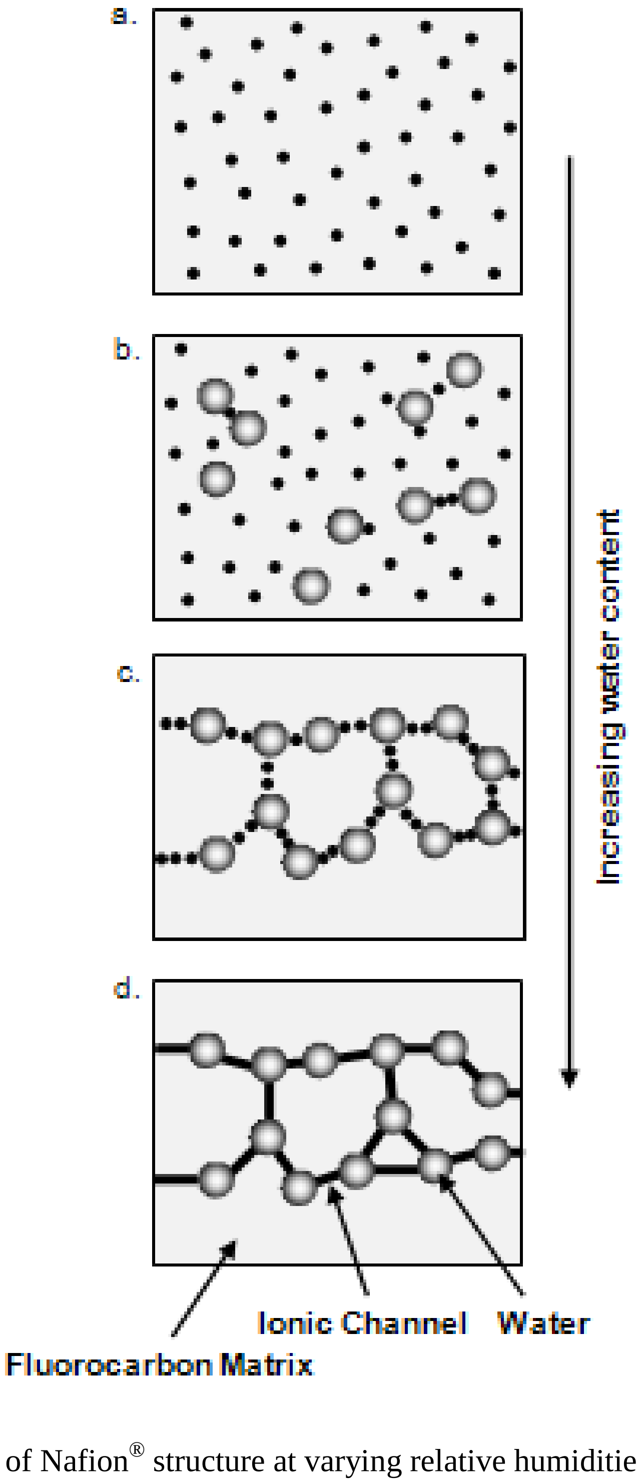

Figure 2.4. Schematic of Nafion® structure at varying relative humidities. Reproduced with permission[13]

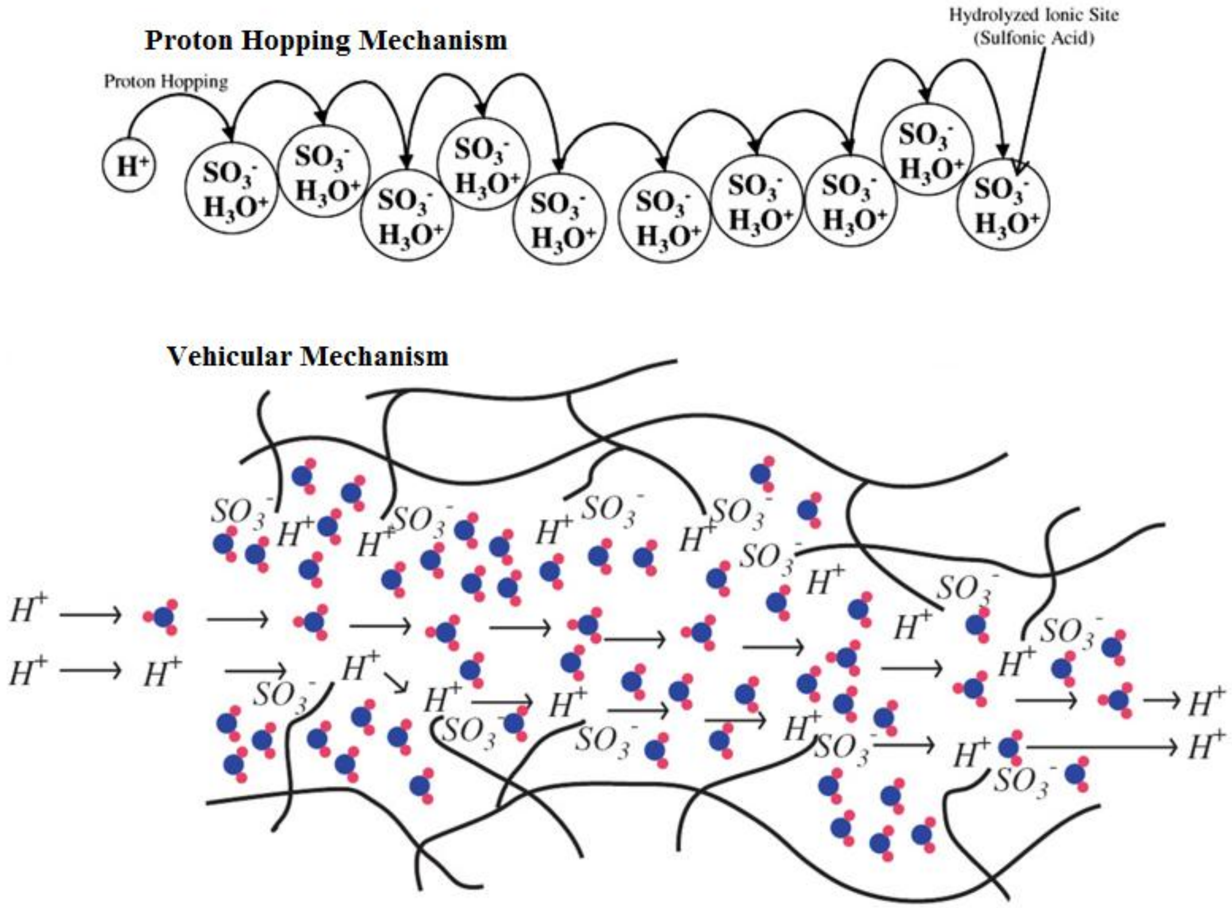

Figure 2.5. Proton transport mechanisms. Reproduced with permission.[10]

to remove heat generated by the fuel cell. Based upon the amount of heat produced by the fuel cell and the ability of the radiator to dissipate this heat, ideal operating conditions are 105 ˚C or higher. Additionally, at temperatures above 120 ˚C traces of carbon monoxide remaining in the hydrogen from its production from fossil fuels no longer poison the platinum catalyst as occurs at lower temperatures.[3] However, with an operating temperature above 80 ˚C, Nafion® membranes become dried out and show reduced conductivity and power output.[3] Thus, the ideal operating conditions for the Nafion® membrane differ from the ideal operating conditions of the fuel cell, requiring new membrane technology that can perform at a higher temperature and lower relative humidity.

The simplest approach to producing a membrane with an increased conductivity is to simply decrease the TFE content of the polymer.[14] While membranes with EWs of 1000-1100 g/mol are useful for chlor-alkali cells where mechanical stability is more important than conductivity due to the membrane being self-supported in water (completely hydrated), membranes in PEMFCs are sandwiched between two electrodes and can sacrifice mechanical strength to increase conductivity. The 3M Company has shown that below a certain EW threshold, 700 g/mol for their monomer (perfluoro-4-(fluorosulfonyl) butyl vinyl ether), the material loses TFE crystallinity and becomes water soluble and useless in a fuel cell.[15] Patent art from W. L. Gore and Associates shows that by using a mini-emulsion to prepare the ionomer, lower TFE contents can be used before water solubility and high swelling are seen.[16]

Unlike most commercial polymerizations that use emulsion techniques exclusively, Nafion® can be prepared using solution polymerization. The main benefit to performing solution polymerizations of PSEPVE and TFE is avoiding use of the toxic and environmentally persistent surfactant, ammonium perfluorooctanoate (PFOA). Typical solvents are either perfluorinated solvents, such as perfluorohexane, or partially fluorinated solvents, such as 2,3-dihydro-decafluoropentane (HFC-4310) or 2H-perfluoro-5-methyl-3,6-dioxanonane (E2). Highly fluorinated solvents are typically chosen for solution polymerizations of PSEPVE for both the solubility of the monomer as well as reduced chain transfer termination reactions. Solvents with a high chain transfer rate, such as hydrocarbons or alkanes bearing a carbon-chlorine bond, give low molecular weight polymers due to the high rate of termination through chain transfer. The use of a highly fluorinated or perfluorinated solvent lowers or removes chain transfer termination mechanisms, respectively.

The free-radical solution polymerization is typically initiated with a diacyl peroxide initiator, such as pentafluoropropionyl peroxide (3P) or hexafluoropropylene oxide dimer peroxide (HFPOdp), which thermally decompose to yield fluorocarbon radicals and carbon dioxide.[1] The first order rate constant for decomposition of 3P is $1.2 * 10^{-5}$ s^{-1} at 25 °C, giving it a half-life of 16 hours.[17] For HFPOdp at 25 °C, a rate constant of $10.0 * 10^{-5}$ s^{-1} is observed, giving a half-life of 1.9 hours.[18] Radical flux is a term used to describe the amount of initiator radicals present in the polymerization at any given time. If it is assumed that the perfluoroalkyl radicals generated from decomposition of 3P and HFPOdp react at a similarly high rate with the monomer in solution, the radical flux is based upon the concentration of the peroxide initiator as well as its half-life. With the half-life being lower for HFPOdp due to the more thermally stable secondary radical formed, a higher radical flux is observed from the same concentration of initiator at the same temperature. As a higher radical flux results in lower molecular weights of product due to the increased rate of termination, lower molecular weight polymers are obtained when HFPOdp is used as the initiator as opposed to 3P under the same conditions.

For copolymerizations, another important variable for consideration is the reactivity ratios of the two monomers. As seen below, the rate constant for a growing polymer chain terminated by Monomer 1 (M1) subsequently adding another M1 is denoted k_{11}. Additionally, the rate constant for M1 adding Monomer 2 (M2) is denoted k_{12}. The reactivity ratio for a growing polymer chain terminated by M1 is then denoted as r_1, the ratio of k_{11} to k_{12}. The reactivity ratio for monomer 2 is calculated similarly by using the rate constants for addition of M1 or M2 monomers to a growing polymer chain terminated by M2. As can be seen from these formulas a reactivity ratio over 1 shows a monomer where the rate of polymerization with itself (homopolymerization) is higher than its rate of polymerization with the other monomer (copolymerization). A reactivity ratio much lower than 1 indicates the rate of polymerization for that monomer is much higher for the co-monomer than itself. Thus, if both reactivity ratios are very low, a copolymer is formed that trends toward an alternating material. If both reactivity ratios are much larger than 1, ether two homopolymers or block copolymers are formed. When one reactivity ratio is much higher than 1 and the other is much lower than 1, a random copolymer is formed.

$$M_1\cdot + M_1 \overset{\boldsymbol{k_{11}}}{\Rightarrow} M_1M_1$$

$$M_1\cdot + M_2 \overset{\boldsymbol{k_{12}}}{\Rightarrow} M_1M_2$$

$$M_2\cdot + M_2 \overset{\boldsymbol{k_{22}}}{\Rightarrow} M_2M_2$$

$$M_2\cdot + M_1 \overset{\boldsymbol{k_{21}}}{\Rightarrow} M_2M_1$$

$$r_1 = \frac{k_{11}}{k_{12}} \qquad r_2 = \frac{k_{22}}{k_{21}}$$

The reactivity ratios for TFE and PSEPVE have not been released by DuPont, Asahi Glass, or Asahi Chem, the world’s major industrial producers of these polymers; however, the reactivity ratios of TFE and PSEPVE have been calculated by several academic groups with values of 9.0 and 0.04 using 1,1,2-trichloro-1,2,2-trifluoroethane as the solvent[19] and 7.85 and 0.079 using supercritical CO_2 as the solvent,[20] respectively. Based on these values it becomes evident that both monomers favor the subsequent addition of TFE units as well as the randomness of the polymer chains. The preparation of low TFE content (low EW), high molecular weight copolymers of TFE and PSEPVE is difficult based upon these values. Growing chains terminated with a PSEPVE unit are over 12 times more reactive towards the subsequent addition of a TFE monomer over another PSEPVE monomer. Growing chains terminated with a TFE unit are nearly 8 times more reactive towards subsequent addition of another TFE monomer over a PSEPVE monomer. Thus, while lowering the concentration of TFE in the reaction will obviously lower the amount of TFE in the polymer, it also lowers molecular weight since the kinetics of addition of a PSEPVE monomer is slow. No matter whether the chain is terminated by a TFE or PSEPVE monomer, the subsequent addition of another PSEPVE monomer is slow, significantly reducing molecular weights for materials with low TFE contents.

Emulsion polymerization techniques are the most common route for producing other fluoropolymers, and these techniques can also be used in the preparation of copolymers of TFE and PSEPVE. Using a sufficient concentration of perfluorinated surfactant above its critical micelle concentration (CMC) in water results in the polymerization actually taking place inside the micelles. The major advantages to this polymerization route are the use of water as a solvent and the higher molecular weights obtained, as no chain transfer agents are present whatsoever. However, a major disadvantage with this route in an academic lab is the lower yield of polymer obtained based on reactor volume. As the amount of PSEPVE that is present within the micelles is fixed and the autoclave contains mostly water, the amount of product that can be obtained from a single polymerization is lower than for solution polymerizations with a constant volume polymerizer.

Emulsion polymerizations of TFE and a sulfonimide version of PSEPVE have been pioneered by the DesMarteau group.[3] Due to the ionic nature of the sulfonimide functional group and the hydrophobicity of the fluorocarbon monomer, self-emulsifying polymerizations have even been performed.[21] Using a 1-liter autoclave and producing polymers having high EWs of 1100-1200, only 11-13 g of polymer are recovered for most runs.[3,22] These materials show increased conductivities at low relative humidity compared to sulfonic acid polymers due to the increased acidity of the sulfonimide functional group.[23] The 3M Company has expanded upon this technology by producing materials where side groups contain both a sulfonimide and sulfonic acid, lowering the equivalent weight while retaining water insolubility.[15]

The nomenclature used for the polymers described throughout this Chapter is University of Alabama eXperimental Resin (UAXR) followed by the sample number. Preparation of the sulfonamide resin gets the nomenclature UAXR1A2, where the number 1 is the polymer number based on the polymerization, A is signifying that the initial sulfonyl fluoride resin has been converted to the sulfonamide, and the number 2 refers to the specific preparation of the sulfonamide resin.

2.2 Experimental

2.2.1 Reagents

All reagents are ACS grade, if applicable, and used as received unless specifically stated otherwise. The PSEPVE monomer, water content of 24 ppm by Karl Fischer, and HFC-4310, water content 51 ppm, are obtained from the DuPont Company. Dow monomer has been obtained from laboratory stock. Pentafluoropropionyl chloride and pentafluoropropionic acid, used to make the TFE detailed in Chapter 1, are obtained from SynQuest Laboratories. Perfluorohexane and HFE-7100 are obtained from the 3M Company.

2.2.2 Original Preparation of Perfluoropropionyl Peroxide (3P)[24]

Similarly to U.S. Patent 2,792,423, to the Schlenk flask of the apparatus shown in Figure 2.6, an amount of 27.4 g of pentafluoropropionyl chloride (b.p. 14 ˚C) is vacuum transferred. One hundred grams of deoxygenated H_2O is poured into the 1.0-L, round-bottomed side of the apparatus, which is then cooled to 0 ˚C, and 7.8368 g of sodium peroxide is slowly added over a 20 minute period with stirring. To this solution is added 500 mL of deoxygenated perfluorohexane as a solvent before cooling to -5 ˚C while bubbling nitrogen through the solution to keep oxygen out. The apparatus is then inverted and the stopcock separating the two sides is opened to allow the perfluoropropionyl chloride to flow into the round-bottomed side of the flask. After two minutes of vigorous shaking, the mixture is poured into a separatory funnel, and the lower layer is drained into the storage vessel seen in Figure 2.7, which is then stored in a freezer at -80 ˚C under 40 psig of nitrogen pressure, again to keep air out. Using the titration method from Example 2.2.6, the solution is found to have a concentration of 0.106 M, producing 3P in 71% yield.

2.2.3 Original Preparation of Perfluorobutyryl Peroxide (4P)[24]

A similar preparation is employed as Example 2.2.2 with 27.80 g of perfluorobutyryl chloride used in place of perfluoropropionyl chloride and the molar ratio of sodium peroxide kept the same with 501 mL of HFC-4310 used as the solvent. Using the titration method described in Example 2.2.6, the initiator solution is found to have a molar concentration of 0.094 M, produced in 79% yield.

Figure 2.6. Apparatus for initiator preparation.

Figure 2.7. Initiator storage container.

2.2.4 Alternative Preparation of Perfluoropropionyl Peroxide (3P)[25]

To the Schlenk flask of the apparatus shown in Figure 2.6, 23.55 g of perfluoropropionyl chloride (b.p. 14 ˚C) is vacuum transferred. Eighty grams of deoxygenated H_2O is poured into the 1-L, round-bottomed side of the apparatus, which is then cooled to 0 ˚C, and 14.49 g of potassium hydroxide is added with stirring. To this solution is added 400 mL of a deoxygenated fluorinated solvent such as 2,3-H-perfluoropentane (HFC-4310), perfluorohexane, or methyl nonafluorobutyl ether (HFE-7100) as a solvent before cooling to -5 ˚C while bubbling nitrogen through the solution to keep out oxygen. An amount of 22.45 mL of 30% hydrogen peroxide is added to the 1-L, round-bottomed side of the flask, and the solution is shaken for 10 seconds before the apparatus is inverted and the stopcock separating the two sides is opened to allow the perfluoropropionyl chloride to flow into the round-bottomed side. After two minutes of vigorous shaking, the mixture is poured into a separatory funnel containing 100 mL of a 5% sodium bicarbonate solution, the lower layer is drained into a second separatory funnel containing 100 mL of a 5% sodium bicarbonate solution, and finally this lower layer is drained into the storage vessel and stored in a freezer at -80 ˚C. Using the titration method from Example 2.2.6, the solution is found to have a concentration of 0.083 M, producing 3P in 52% yield.

2.2.5 Preparation of Hexafluoropropylene Dimer Peroxide (HFPOdp)[25]

A sample of hexafluoropropylene dimer acid fluoride (HFPOdaf) contaminated with acetonitrile was obtained from the DuPont Company. The sample is placed over concentrated sulfuric acid overnight before the volatiles are vacuum transferred to a new vessel with the resulting material having less than 1 mol% acetonitrile by ^{13}C NMR spectroscopy. Using the same procedure as Example 2.2.4, purified HFPOdaf is converted into hexafluoropropylene oxide dimer peroxide (HFPOdp) with a concentration of 0.16 M in perfluorohexane.

2.2.6 Titration of Diacyl Peroxide Initiators[26]

Similar to the peroxide titration in U.S. Patent 5,021,516, an amount of 25 mL of glacial acetic acid and several dry ice pellets are added to a Schlenk flask with 3.0 g of potassium iodide in 5.0 mL of water. Using a pipette, 5.0 mL of the previously prepared initiator solution is added and allowed to stir in the lightly sealed Schlenk flask for 30 minutes at room temperature before adding 100 mL of deoxygenated water. The deep orange color is then titrated to colorless using a 0.10 M sodium thiosulfate solution. Care is taken to keep oxygen out at all steps in order to achieve high precision and accuracy, and the titrations are performed in triplicate.

2.2.7 Solution Polymerization of UAXR8

Both the PSEPVE monomer and HFC-4310 are degassed on a vacuum line through the freeze/pump/thaw method to remove oxygen. In a dry box 384.16 g of PSEPVE and 341.54 g of HFC-4310 are added to the 600-mL stainless steel autoclave that has been pacified with concentrated nitric acid. The autoclave is attached to the system flex tubing and all new connections are leak checked before evacuating and back-filling with nitrogen three times. The autoclave is heated to 35 ˚C at a stirring rate of 200 rotations per minute (RPM). Using the ISCO® pump, the initiator line is filled and washed twice with 10 mL of a 0.147 M solution of 3P in HFC-4310 before adding 10 mL of the solution to the autoclave over 1 minute and then reducing the flow rate to 0.0166 mL/min for the next 2 hours 19 minutes. As seen in Figure 2.8, the equimolar mixture of TFE and CO_2 is continuously added to the autoclave using the system described in Chapter 1 as the TFE is consumed. Workup is performed by removing the autoclave from the system, venting in a hood, pouring the resin into a resin kettle, and removing all volatile products up to 150 ˚C and 50 mtorr to yield 96.14 g polymer with an EW of 1000 g/mol by IR spectroscopy and titration.

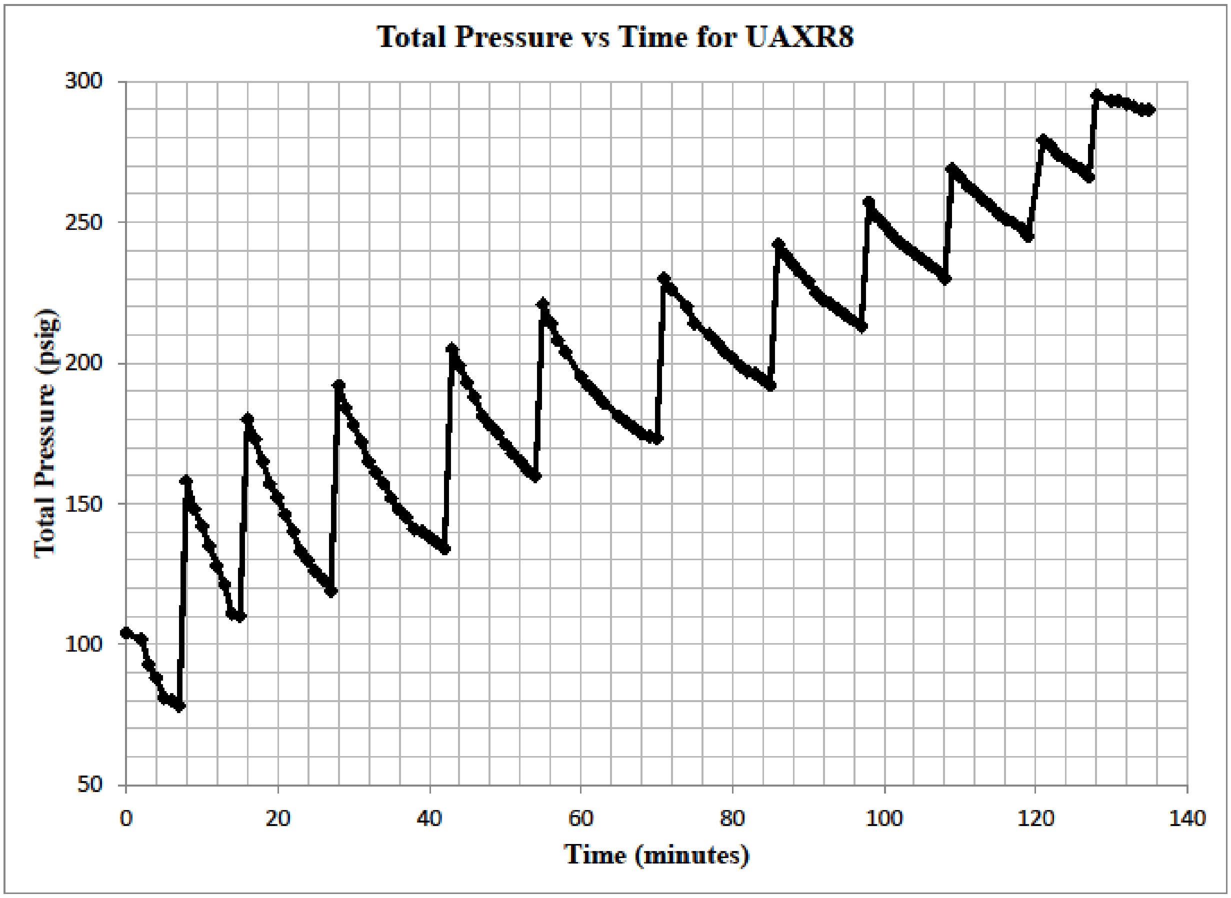

Figure 2.8. Total pressure vs. time for polymerization UAXR8.

ATR-FTIR Analysis (cm^{-1}) of UAXR8: 1465 (s); 1314 (w); 1237 (w); 1188 (s); 1131 (s); 983 (s); 821, 798 (doublet, m).

Representative solution polymerization, see Table 2.1 for full list of solution and bulk polymerizations performed.

2.2.8 Solution Polymerization of UAXD6

In a dry box, 249.61 g of Dow and 537.82 g of HFC-4310, previously deoxygenated by the freeze/pump/thaw method, are added to the 600-mL SS autoclave. After attachment to the system and setup similar to Example 2.2.7, 14.0 mL of a 0.0983 M solution of 3P in HFC-4310 is added over two minutes followed by a slow feed of 0.0389 mL/min for 5 hours 2 minutes. During that time the TFE and CO_2 mixture is added to the autoclave as seen in Figure 2.9. Workup is performed similarly to Example 2.2.7, yielding 64 g of polymer with an EW of 700 g/mol by titration, as described in Example 2.2.20.

2.2.9 Bulk Polymerization of UAXR15

To the 100-mL stainless steel autoclave is added 149.42 g of degassed PSEPVE and attached to the system and setup as Example 2.2.7 except with a temperature of 45 ˚C. Using the ISCO pump, 2.3 mL of a 0.2324 M solution of 4P in perfluorohexane is added to the polymerization vessel over 1 minute before pressurizing the autoclave to 55 psia with an equimolar mixture of TFE and CO_2 and having a stirring rate of 200 RPM. The polymerization is then allowed to react overnight as the TFE is consumed and the pressure drops. Workup is performed similarly to Example 2.2.7 yielding 14.94 g of polymer with an EW of 500 g/mol by infrared spectroscopy as described in Example 2.2.19. Representative bulk polymerization with CO_2, see Table 2.1 for full list of solution and bulk polymerizations performed.

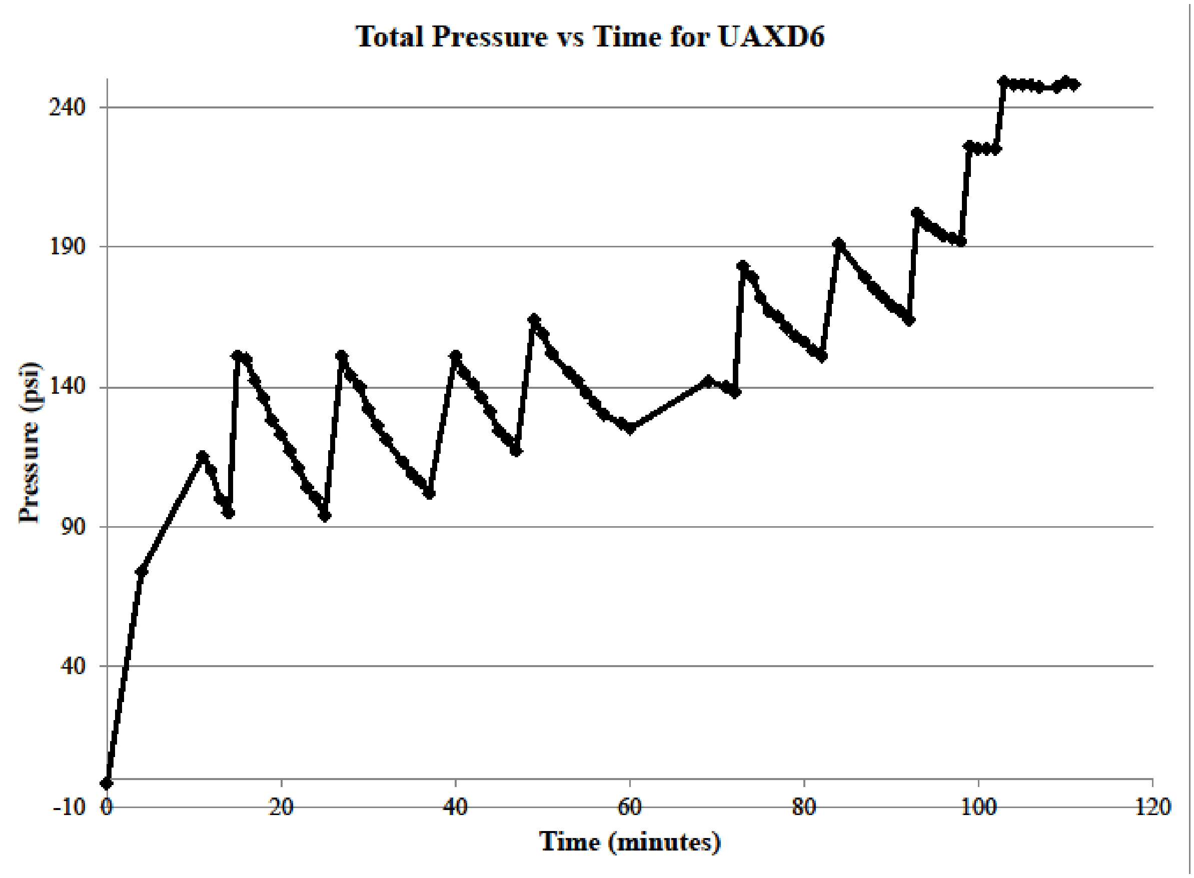

Figure 2.9. Total pressure vs. time for polymerization UAXD6.

2.2.10 Bulk Polymerization of UAXR16

After adding 128 g of degassed PSEPVE to the 100-mL stainless steel autoclave, the reaction vessel is attached to the system and setup as in Example 2.2.7. With the CO_2 scrubber installed, the TFE and CO_2 mixture is slowly added to the autoclave taking care never to allow the temperature on the six point thermocouple located in the scrubber to reach above 50 ˚C. The pressure of neat TFE inside the autoclave head space is kept at 55 psia throughout the reaction with a stirring rate of 200 RPM. Using the ISCO® pump, 4.0 mL of a 0.106 M solution of 3P in perfluorohexane is added to the polymerization vessel over 1 minute followed by 5 hours of a 0.00667 mL/min addition rate. After overnight reaction, workup is performed similarly to that in Example 2.2.7 yielding 14.94 g of polymer with an EW of approximately 550 g/mol by infrared spectroscopy as described in Example 2.2.19.

$\{CF_2^aCF^b[OCF_2^cCF^d(CF_3^e)OCF_2^fCF_2^gSO_2F^h]\}_n\{CF_2^zCF_2^z\}_m$ ^{19}F NMR spectrum for UAXR16 in R113: δ^a -119.0; δ^b -139.9 (broad); δ^c -79.9; δ^d -145.5; δ^e -81.2; δ^f -80.4; δ^g -113.7; δ^z -120.8, -121.7, -122.5.

Representative bulk polymerization without CO_2, see Table 2.1 for full list of solution and bulk polymerizations performed.

2.2.11 Emulsion Polymerization UAXE3 with CO_2 Present

To a 600-mL stainless steel autoclave washed with nitric acid is added 0.7190 g of sodium bisulfite, 3.9829 g of sodium dihydrogen phosphate monohydrate, 6.8500 g of sodium hydrogen phosphate, 5.0904 g of PFOA, 8.2679 g of PSEPVE, and 352.26 g of H_2O. The solution is degassed to remove oxygen and then attached to the polymerization system similarly to Example 2.2.7. While stirring at a rate of 550 RPM, the autoclave is heated to 60 ˚C before 50 mL of a 0.10 M solution of ammonium persulfate in water is added. The pressure of TFE and

Table 2.1. Solution and Bulk Copolymerizations of TFE and PSEPVE/Dow

Sample	Monomer (g)	HFC-4310 (g)	Initiator (mmol)	Product (g)	TFE/CO2 Mixture Added (g)	EW (g/mol)
UAXR1	164	415	0.752	8	18.2	700
UAXR2	150	400	0.897	14	X	850
UAXR4	401	361	2.093	100	93	900
UAXR5	50 (DowA)	675	0.7372	0	29	-----
UAXD6	250 (Dow)	538	2.064	60	79	700
UAXR7	35 (DowA)	640	0.302	5	55	-----
UAXR8	384	342	2.205	96	102	1000
UAXR9	403	350	2.205	137	146	1000
UAXR10	547	203	2.925	94	109	1000
UAXR11	65	-----	0.329	0.18	10	-----
UAXR13	65	-----	0.7	2.01	15	550
UAXR14	148.75	-----	0.698	7.0	5.1	600
UAXR15	149.42	-----	0.535	14.94	110 psig Mixture	500
UAXR16	128	-----	0.636	19.08	40 psig Neat TFE	550
UAXR17	85.01	-----	0.321	9.68	35 psig Neat TFE	550

CO_2 is increased to 135 psia and the reaction proceeds for 4 hours 40 minutes before turning off the heater, at which point the total pressure in the system is 120 psia. Workup is performed by adding 12 M HCl to the latex until disruption of the micelles causes precipitation of the product polymer. Fifteen water washes are performed on the polymer to remove most of the PFOA, yielding 11.79 g polymer with an EW of 800 g/mol by IR spectroscopy.

$\{CF_2^aCF^b[OCF_2^cCF^d(CF_3^e)OCF_2^fCF_2^gSO_2NH_2]\}_n\{CF_2^zCF_2^z\}_m$ ^{19}F NMR spectrum for UAXE3A1 (prepared similarly to Example 2.2.14) in ACN-d3: δ^a -118.1; δ^b -138.6, -137.2 (depending on arrangement); δ^c -78.7; δ^d -144.2; δ^e -80.1; δ^f -79.0; δ^g -117.1; δ^z -120.9, -121.8.

2.2.12 Emulsion Polymerization UAXE4 with Neat TFE

To a 600-mL stainless steel autoclave pickled by washing with nitric acid is added 0.7286 g of sodium bisulfite, 4.0294 g of sodium dihydrogen phosphate monohydrate, 6.9026 g of sodium hydrogen phosphate, 5.0230 g of PFOA, 8.3026 g of PSEPVE, and 352.26 g of H_2O as seen in Table 2.2. The polymerization is setup similarly to Example 2.2.11 except an Ascarite® scrubber is added to the system to remove CO_2. With valve TFE3 closed, the system is pressurized to 85 psia of neat TFE after the BPR. After 19 mL of a 0.279 M solution of ammonium persulfate in deoxygenated DI water is added using the ISCO® pump, valve TFE3 is opened allowing neat TFE to flow into the autoclave and the pressure is maintained at 75 psia as the reaction progresses. After 4 hours and 40 minutes the heat to the autoclave is turned off and the reaction is allowed to sit overnight. Workup is performed the same as example 2.2.10, yielding 7.89 g of polymer with an EW of approximately 600 g/mol by IR spectroscopy.

$\{CF_2^aCF^b[OCF_2^cCF^d(CF_3^e)OCF_2^fCF_2^gSO_2NH_2]\}_n\{CF_2^zCF_2^z\}_m$ ^{19}F NMR spectrum for UAXE4A1 in ACN-d3: δ^a -117.7; δ^b -137.0, -138.4 (depending on monomer arrangement); δ^c -78.6; δ^d -144.1; δ^e -79.9; δ^f -78.9; δ^g -117.0; δ^z -119.4, -120.7, -121.5.

Table 2.2. Emulsion Copolymerization of TFE and PSEPVE

Sample	PSEPVE (g)	PFOA (g)	NaH_2PO_4 (g)	Na_2HPO_4 (g)	$NaHSO_3$ (g)	$(NH_4)_2S_2O_8$ (g)	TFE (psig)	Temp ˚C	Polymer (g)	EW (g/mol)
UAXE1	7.53	4.97	3.93	7.01	0.70	1.13	125	10 1 hour, then 60	5.67	750
UAXE2	8.07	4.96	3.52	4.63	0.79	1.19	75	60	-----	-----
UAXE3	8.11	5.07	3.98	6.85	0.72	1.25	120	60	11.8	800
UAXE4	8.19	5.01	4.03	6.90	0.72	1.21	60 (neat TFE)	60	7.9	600

2.2.13 Solution Amidation of UAXR10 to Produce UAXR10A1

An amount of 6.52 g of UAXR10 is dissolved in refluxing perfluorohexane previously dried over P_2O_5 (H_2O content less than the 10 ppm detection limit by Karl Fischer titration). To a 2-necked round-bottomed flask equipped with a dry ice condenser and an inlet tube, ammonia is bubbled through the solution to maintain a high reflux rate for several hours. The ammonia is allowed to boil away and the volatiles, including ammonium fluoride, are all removed by heating to 110 ˚C at 50 mtorr. Acetonitrile dried over calcium hydride (H_2O content less than the 10 ppm detection limit of the instrument) is then added to the flask and heated to refluxing. After three extractions with acetonitrile, 5.67 g of white product is obtained in 87% yield.

$\{CF_2^aCF^b[OCF_2^cCF^d(CF_3^e)OCF_2^fCF_2^gSO_2NH_2]\}_n\{CF_2^zCF_2^z\}_m$ ^{19}F NMR spectrum for UAXR10A1 in ACN-d3: δ^a -117.6; δ^b -138.1 (broad); δ^c -77.9; δ^d -144.4; δ^e -79.5; δ^f -78.2; δ^g -116.8; δ^z -121.4.

2.2.14 Gas Phase Amidation of Low Surface Area UAXR10 to Produce UAXR10A2[27]

In a nickel autoclave is placed 4.00 g of UAXR10 resin and 45 psia ammonia is added to the solid polymer while the decrease in pressure is monitored and adjusted every hour. Again the ammonium fluoride is removed by sublimation and the product is extracted several times with refluxing acetonitrile to yield 2.52 g of white sulfonamide polymer in 63% yield.

2.2.15 Gas Phase Amidation of High Surface Area UAXR10 to Produce UAXR10A3[27]

An amount of 4.20 g of UAXR10 is cryogrinded to yield micron sized particles with a higher surface area than the resin in Example 2.2.14. Ammonia additions and workup are performed similarly to Example 2.2.14 yielding 3.23 g of white product in 77% yield.

2.2.16 High Temperature Gas Phase Amidation of Low Surface Area UAXR10 to Produce UAXR10A4[27]

Into a Monel autoclave is placed 4.02 g UAXR10 sliced into strips and subsequently heated to 60 ˚C and pressurized to 45 psia with ammonia and the decrease in pressure monitored as the ammonia is consumed. A similar workup to Example 2.2.13 is followed, giving a material that is completely insoluble in acetonitrile and green in color.

2.2.17 Amidation of PSEPVE

To a two-necked, round-bottomed flask equipped with a pressure-equalizing addition funnel and a condenser, 50.38 g of PSEPVE is slowly added to 113.75 g of a 1.0 M lithium hexamethyldisilazane (LHMDS) in THF solution and 51.63 g of hexane in an ice bath. After complete addition of the PSEPVE, the solution is allowed to warm to room temperature, at which time 100 mL of 1.2 M HCl is slowly added before heating to 35 ˚C under a nitrogen pad to remove the hexane. Five extractions are performed with HFC-4310 to isolate the product. Distillation of the product gives 37.03 g of the sulfonamide version of PSEPVE in 74.0% yield.

2.2.18 Preparation of ^{15}N Enriched UAXR8A

Formation of ^{15}N enriched UAXR8A is performed by dissolving 2.47 g of UAXR8 in 105.29 g of perfluorohexane inside a round-bottomed flask. Using vacuum line techniques, three equivalents of 10% enriched $^{15}NH_3$ is added overnight. Theoretical weight gain from complete conversion from sulfonyl fluoride to sulfonamide, based upon an EW of 1000 g/mol and the assumption that all HF generated reacts with ammonia to form ammonium fluoride, is 0.101 g and an actual weight gain of 0.14 g is observed. The volatile products are then removed by vacuum distillation up to 100 ˚C and 50 mtorr and the remaining solids are dissolved in dry acetonitrile yielding 1.98 g of 10% enriched ^{15}N UAXR8A with IR spectrum seen in Figure 2.10.

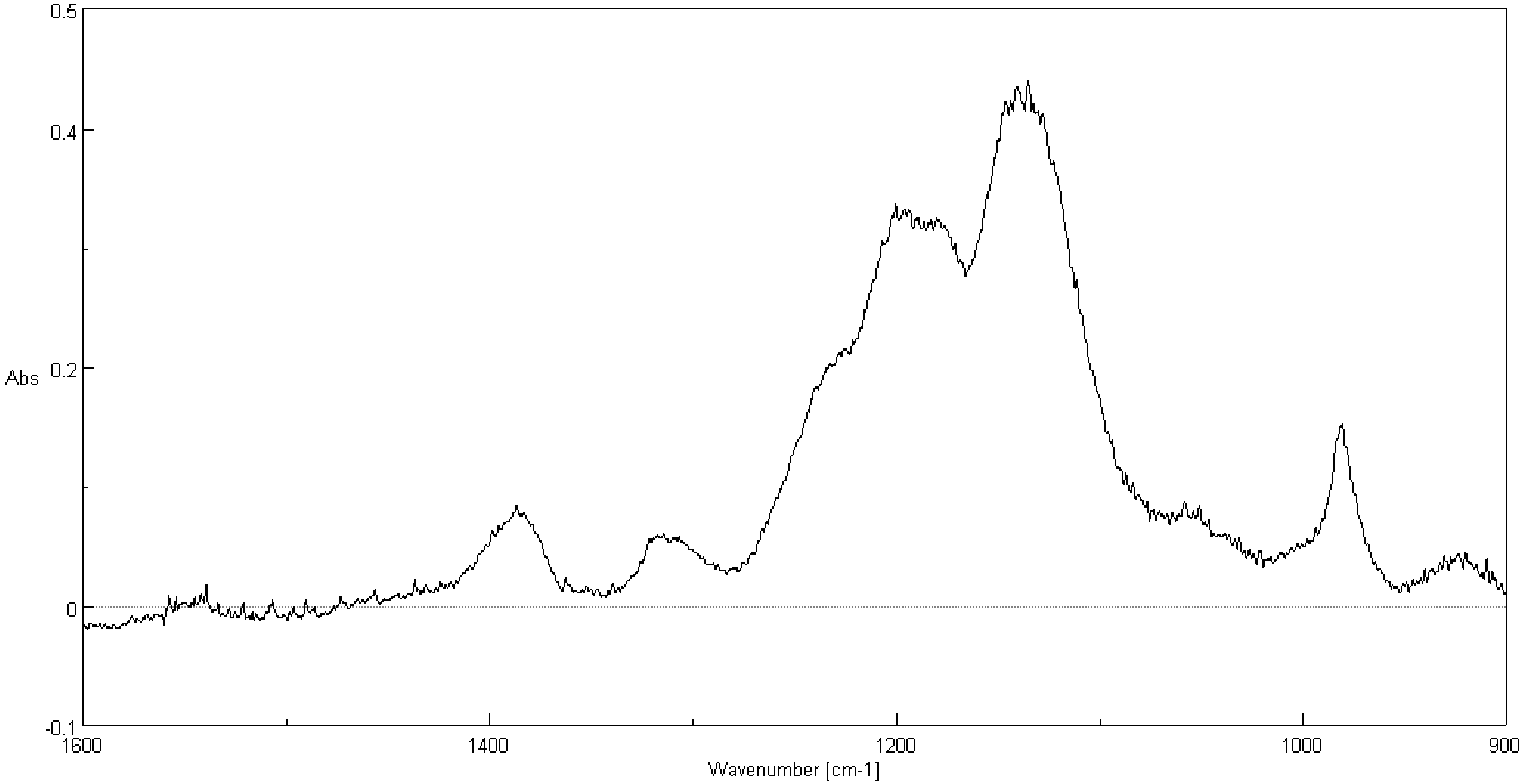

Figure 2.10. ATR-FTIR spectrum of UAXR8A1.

2.2.19 Equivalent Weight Determination by IR Spectroscopy

Equivalent weights are determined by IR spectroscopy using a JASCO FTIR-4000 spectrometer utilizing attenuated total reflectance (ATR-FTIR) and comparing the area under the S-F peak at 1450 cm^{-1} to the C-F stretches from 1100 cm^{-1} to 1300 cm^{-1} as explained in literature reports.[28]

2.2.20 Equivalent Weight Determination by Titration

Samples are hydrolyzed using a 60 ˚C solution of 15% KOH, 35% DMSO, and 50% H_2O by weight Water washes are performed until the decanted liquid is neutral by litmus paper, and then the material is acidified by washing twice in dilute HNO_3 and then immersed in 15 M HNO_3 for 1 hour at 80 ˚C. The membranes are washed in DI water until the decanted liquid is neutral by litmus paper and then dried overnight in a vacuum desiccator at 150 ˚C and 100 torr. A known excess of 0.01 M NaOH solution is added to 100 mg of dried polymer and allowed to sit overnight to react to completeness. Aliquots of 10.00 mL of the resulting solution are back-titrated with 0.01 M potassium hydrogen phthalate (KHP) to determine the moles of acid groups present in the polymer. The equivalent weight (EW) is simply the grams of polymer used divided by the moles of acid sites.

2.2.21 MALDI-TOF MS Analysis

Analysis of sulfonamide resins by matrix assisted laser desorption ionization time of flight (MALDI-TOF) mass spectrometry (MS) is performed using a Bruker Ultraflex TOF instrument by dissolving 20 mg of resin in 1 mL of acetonitrile. An aliquot of 10 microliters from this solution is mixed with 100 microliters of a solution of 7.5 mg/mL of 2,5-dihydroxy-benzoic acid (DHB) in a 50 : 50 acetonitrile : water (v/v) containing 0.1 wt% trifluoroacetic acid (TFA) . Onto a stainless steel MALDI-TOF plate is spotted 30 microliters of this final mixture, which is allowed to dry before analysis. Analysis of hydrolyzed sulfonate resins by MALDI-TOF MS is performed similarly except the original matrix solvent contains water with no acetonitrile.

2.2.22 Thermal Gravimetric Analysis

Thermal gravimetric analysis (TGA) is performed on 15 - 50 mg samples using a TA Instruments TGA 9250 under a nitrogen purge. Samples are typically heated to 120 ˚C and allowed to sit for 1 hour to remove any residual water or solvents present from handling in the laboratory prior to heating to 600 ˚C at a rate of 5 ˚C/min.

2.3 Results and Discussion

2.3.1 Solution and Bulk Polymerizations of TFE and PSEPVE/Dow

Over the course of this research, fifteen solution copolymerizations of TFE with PSEPVE or Dow have been prepared as shown in Table 2.1. Runs UAXR1 through UAXR10 focused mainly on increasing yields of polymer while producing samples with EWs only slightly lower than commercial Nafion®. With 137 g of product from a 600-mL autoclave for polymerization UAXR9, these solution polymerizations are shown to give much higher yields than the comparative emulsion polymerizations performed by the DesMarteau group.[3] An important finding in the polymerizations is the importance of adequately removing oxygen from the initiator solution on top of the monomer solution. By using an initiator solvent that has been deoxygenated by the freeze/pump/thaw method, higher yields and molecular weights are seen. Additionally, storing the initiator inside the vessel shown in Figure 2.7 under nitrogen pressure and always keeping a nitrogen pad on the solution while the storage vessel is open ensures the absence of oxygen and the ability to obtain higher yields.

One non-ideal portion of these polymerizations is the use of the mixture of TFE with CO_2. While this mixture adds safety to the project, it adds difficulty in controlling equivalent weights. The weight difference in the TFE/CO_2 storage cylinder before and after polymerization for run UAXR9 is 146 g. Adding this large a quantity of CO_2 to the Ascarite® scrubber is impractical based both on the cost of the Ascarite® and volume of the scrubber. Additionally, based upon how quickly the TFE is consumed and must be replaced, it is dangerous to flow this much TFE through the scrubber with the exothermic reaction possibly causing unsafe temperatures. Performing these polymerizations with the CO_2 present causes an increase in the vapor space pressure over the course of the polymerization. As TFE is consumed in the reaction more TFE and CO_2 gas is added; however, the CO_2 diluent does not get consumed and as more of the mixture is added over the course of the polymerization, the pressure of the system increases over time. This increase in pressure makes it difficult to control the amount of TFE added into the polymer as a constant pressure of TFE gas cannot be used and the partial pressure of TFE in the reaction is difficult to determine and control.

The second set of polymerizations, UAXR11 through UAXR17, focuses on preparing low EW samples. As expected based upon the reactivity ratios, starving the polymerization of TFE is required to obtain lower EW (less than 4 TFE monomers per PSEPVE monomer on average in the polymer) samples since the reactivity ratios of both TFE and PSEPVE favor reaction with additional TFE monomers. As the reactivity of TFE towards free-radicals is so high and PSEPVE is lower, the only way to decrease the EW significantly is to severely limit the collision frequency of TFE monomer with propagating chains by running at low TFE partial pressures. This has the drawback that molecular weights tend to be very low for the materials since the rate of adding PSEPVE monomers is slow.

It has been found CO_2 should be removed to produce acceptable yields of low EW polymers. Polymerization UAXR15 with 125 psia of TFE and CO_2 gave 10% yield with an EW of 500 g/mol. Alternatively, sample UAXR16 with 55 psia of neat TFE gave 15% yield with an EW of 550 g/mol, close to a 1:1 product. These increased yields and quality of product could be due to CO_2 slowing the rate of polymerization. It is hypothesized that CO_2 slows the kinetics of polymerization by forming the transient carboxylic acid radical (which could also explain how the presence of CO_2 limits the chance for explosive deflagrations of TFE); however, rigorous kinetic measurements have not been performed to determine the rates of polymerization with and without CO_2. Alternatively, with CO_2 present, it could be that the vapor space of the autoclave becomes a CO_2 rich environment instead of staying an equimolar mixture, causing the concentration of TFE in the reaction to decrease significantly. Still, yields and molecular weights are low for the materials even when the CO_2 is removed from the TFE due to the reactivity of adding PSEPVE monomers being so low.

As previously shown by 3M, higher EW samples with an increased ratio of TFE to PSEPVE show water insolubility due to the high crystallinity.[15] By decreasing the ratio of TFE to PSEPVE a more amorphous and less crystalline polymer is produced that becomes water soluble after hydrolysis. The work done by the 3M Company only shows that below an EW of approximately 780 g/mol, crystallinity begins disappearing and approximately 20% solubility is seen at 700 g/mol.[15] This work is presumably based upon their proprietary monomer (3M), which has a molecular weight of 380 g/mol. Sample UAXD6 is prepared with the Dow monomer, which has a lower molecular weight than 3M's monomer, and titrations show an EW of 700 g/mol. However, none of the sample is soluble in the hydrolysis solution or DI water up to 100 ˚C for 12 hours. This shows that the solubility is based upon the ratio of TFE to co-monomer and not on EW alone, suggesting that EWs can be lowered further by producing lower molecular weight co-monomers or increasing the number of acid sites per chain, work performed by the 3M Company as well.[15]

2.3.2 Emulsion Polymerizations of TFE and PSEPVE

Three successful emulsion polymerizations have been carried out producing materials with equivalent weights between 600 and 800 g/mol. Conditions are similar to those used by the DesMarteau group with the main differences being use of lower TFE pressures and an operating temperature of 60 ˚C instead of 10 ˚C. The higher polymerization temperature likely causes lower molecular weight samples due to increased rates of termination by increasing radical flux and β-scission termination; however, high yields of polymer are still obtained with low EWs. Samples UAXE1 and UAXE3 are prepared using the equimolar mixture of TFE and CO_2, a novel approach. The pH of emulsion polymerizations must be carefully controlled to prevent disruption of the micelles and precipitation of the polymer and monomers during the reaction. Reaction of CO_2 with water to yield carbonic acid and lowering the pH may be expected to disrupt micelle formation and terminate the polymerization; however, a total yield of 81.8% is seen for UAXE3 even when taking into account the EW and extra weight of TFE added. Thus, it has been shown that using this phosphate buffer system to control the pH, emulsion polymerizations can be performed with the safer TFE and CO_2 mixture. This discovery opens the possibility to safely undertake many other polymerizations of TFE in the presence of CO_2 using emulsion techniques that are much more common for other fluoropolymers.

Polymerization of sample UAXE4 involves scrubbing CO_2 out of the TFE to allow both a better control of the amount of TFE added and produce a lower EW sample. Holding the pressure of TFE constant at 60 psig produces a sample with an EW of roughly 550 - 600 g/mol based on ^{19}F NMR and IR spectroscopies. While a lower yield of polymer is produced than the initial monomer added into the emulsion, yields are typically reduced for low EW samples due to starving the system of TFE. ^{19}F NMR spectroscopy of the sulfonamide resin dissolved in acetonitrile, shown below in Figure 2.16 (*vide infra*), shows a small broad peak present at -122 ppm, the same region as bulk TFE is typically seen. The IR spectrum shows a peak at 1237 cm^{-1} that is less intense than the corresponding spectrum of poly(PSEPVE) (to be discussed further in Chapter 3) but much more intense than that in high EW samples such as Nafion® 1100.

2.3.3 Sulfonamide Copolymers

Conversion of UAXR samples with sulfonyl fluoride functional groups to the sulfonamide moiety, UAXRA, has been attempted by four different routes. While dissolving the sample in perfluorohexane and bubbling ammonia in gives the highest isolated yield based on the soluble polymer, the solubility of the polymers in perfluorohexane varies between different samples and even slightly within a sample due to the materials not being perfectly uniform. Solid-gas phase reactions prove to be the best route showing high yields even for polymer samples that are not highly soluble in perfluorohexane using a simpler, less expensive, and more easily scalable reaction. By increasing the surface area through cryo-grinding, even higher yields of soluble UAXRA resin could be obtained. Increasing the temperature of the reactions results in a green material, likely from contamination from corrosion of nickel and/or copper from the Monel autoclave; the bulk material as well as the green color, is completely insoluble in refluxing acetonitrile.

Complete conversion of the sulfonyl fluoride resin is verified by both IR and NMR spectroscopies. Disappearance of the intense S-F peak at 1450 cm^{-1} and appearance of the new peak at 1386 cm^{-1} in the infrared spectrum confirms the bulk of the sample has been converted to sulfonamide.[29] Analysis of the soluble samples by ^{19}F NMR spectroscopy, as seen in Figure 2.11, verifies the absence of any S-F stretches at +42 ppm. Any water present during the reaction will convert ammonia to ammonium hydroxide, yielding hydrolysis. The signal for fluorine atoms of the CF_2 group in $R_fCF_2SO_2NH_2$ appears at -117.0 ppm compared to -116.5 ppm for $R_fCF_2SO_3H$, allowing for quantification of the amount of hydrolysis present during and/or after amidification.

Preparation of 10% enriched ^{15}N samples of the sulfonamide allows further analysis by ^{15}N NMR spectroscopy where the peak of the sulfonamide nitrogen appearing at a chemical shift of 84.7 ppm (using liquid ammonia as a reference), as seen in Figure 2.12, matches well with literature reported values for $CH_3SO_2NH_2$ and $PhSO_2NH_2$ of 95.9 ppm and 92.8 ppm, respectively.[30] One concern during the reaction is crosslinking chains through a sulfonimide functional group may be possible; however, no evidence of sulfonimides is seen in the IR spectrum, seen at wavelengths around 1340 cm^{-1}, or in the ^{15}N or ^{19}F NMR spectra.[29]

Perfluorinated polymers are typically not soluble in organic medium due to being highly non-polar. According to literature reports, the maximum EW for solubility of Nafion® type polymers is 900 in mixtures of water and organic solvents.[1] Polymers with EWs above 900 g/mol require temperatures of around 240 ˚C to form what is more likely a dispersion than solution.[1] Here, the sulfonamide version of even Nafion® 1100 shows sufficient solubility in refluxing ethanol to obtain a ^{19}F NMR spectrum as shown in Figure 2.13. Sample UAXR8A1 shows a similar ^{19}F NMR spectrum as Nafion® 1100 sulfonamide except for a few impurities peaks that have not been identified. As shown in Figures 2.13, 2.14, 2.15, and 2.16, the intensity of the peak at -121 ppm attributed to bulk CF_2 groups from TFE decreases with lowering EW up until a point at which there is no longer a single broad peak but up to four different peaks, such

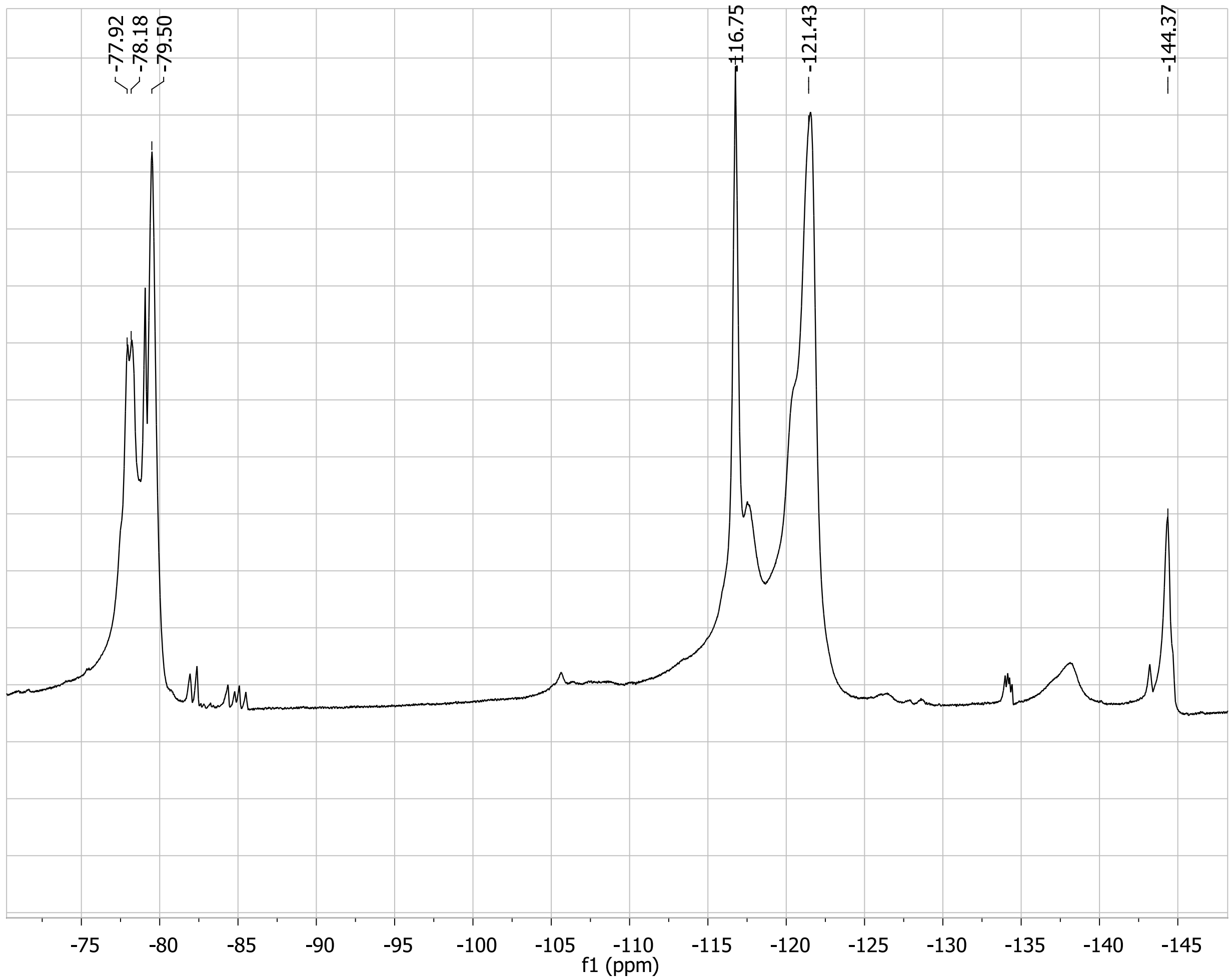

Figure 2.11. ^{19}F NMR spectrum of UAXR8A1 dissolved in acetonitrile. (Representative spectrum of all high EW UAXRA samples.)

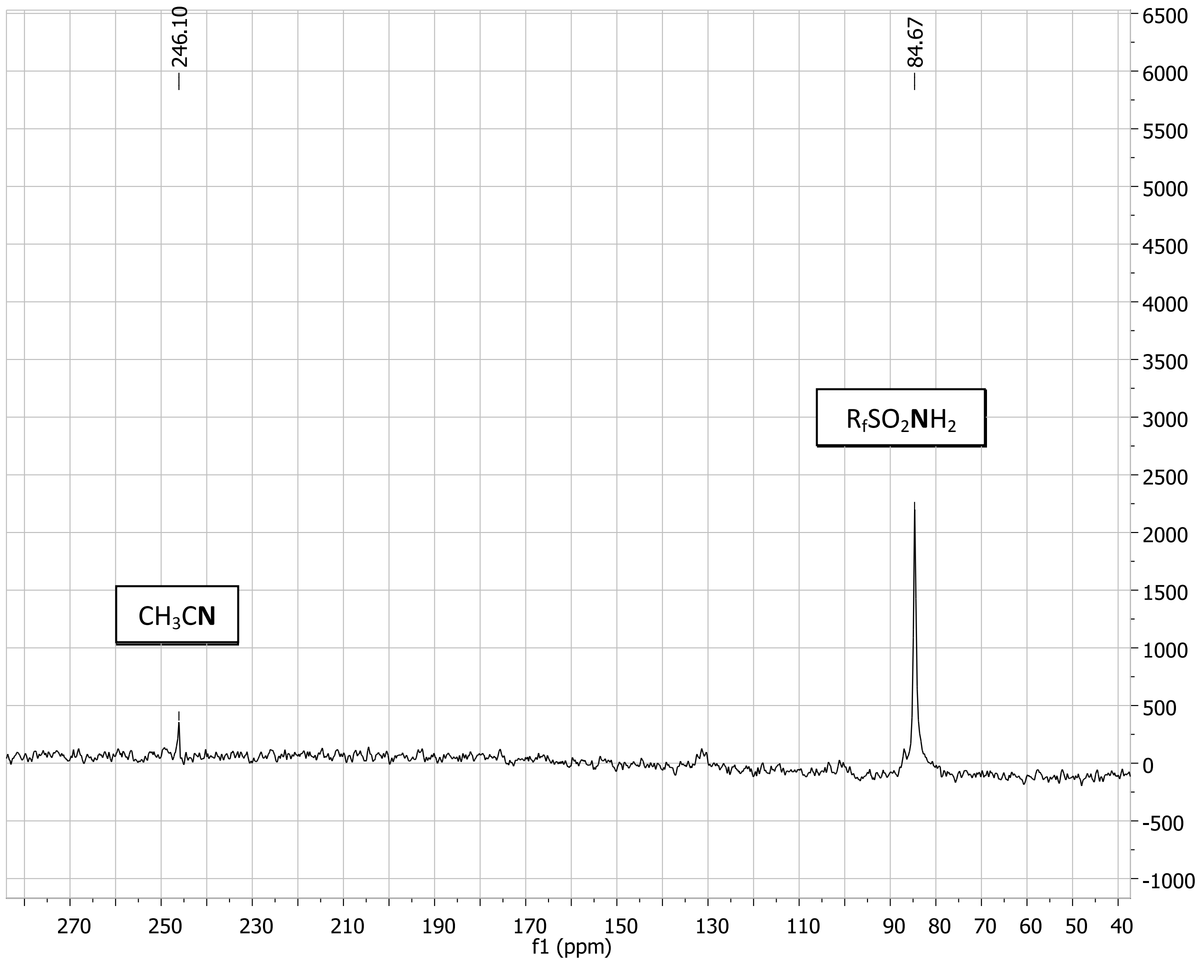

Figure 2.12. ^{15}N NMR spectrum of 98% ^{15}N Enriched UAXR8A1 dissolved in acetonitrile-d3.

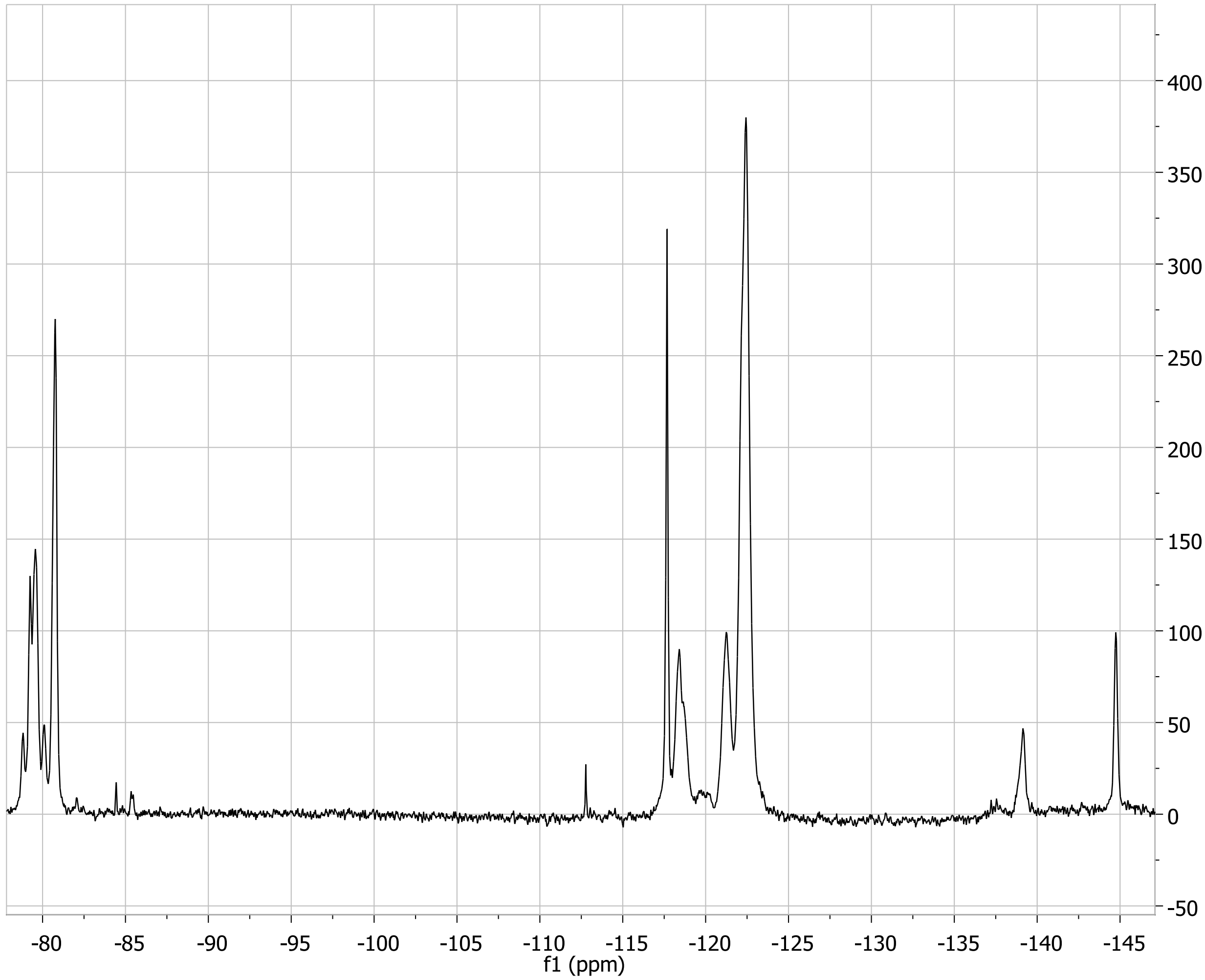

Figure 2.13. ^{19}F NMR spectrum of Nafion® 1100 sulfonamide dissolved in ethanol.

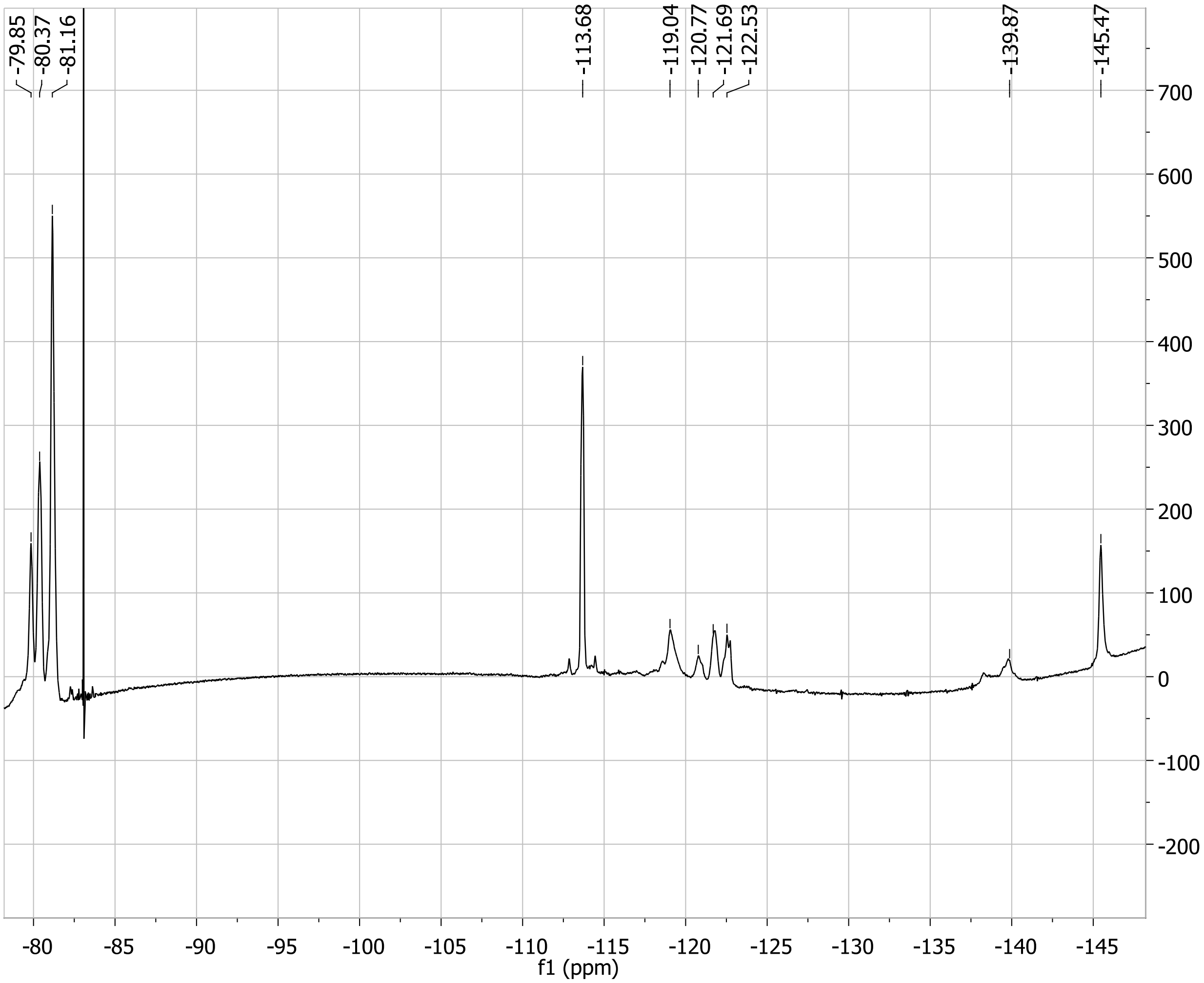

Figure 2.14. ^{19}F NMR spectrum of UAXR16 dissolved in R113.

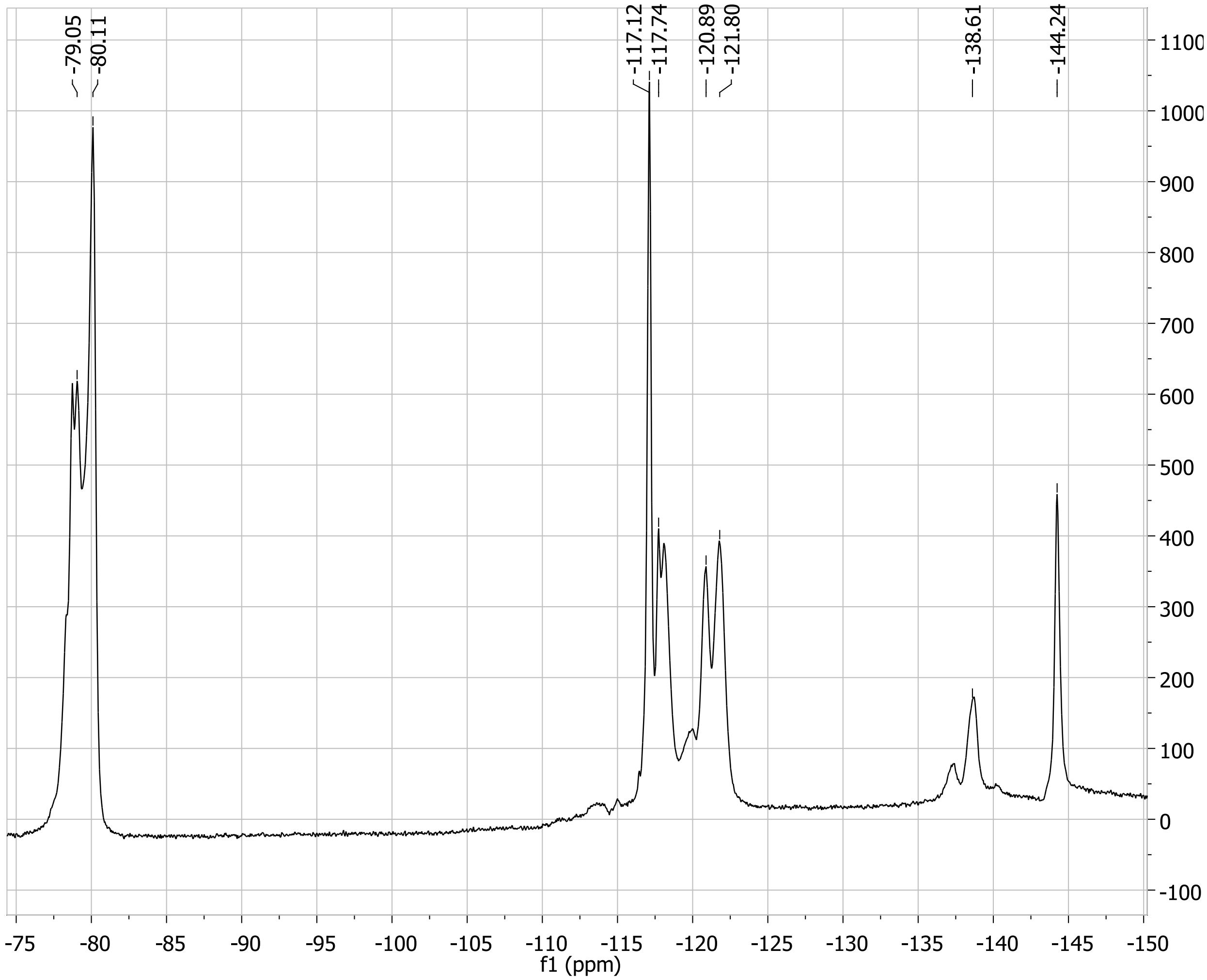

Figure 2.15. ^{19}F NMR spectrum of UAXE3A1 dissolved in acetonitrile-d3.

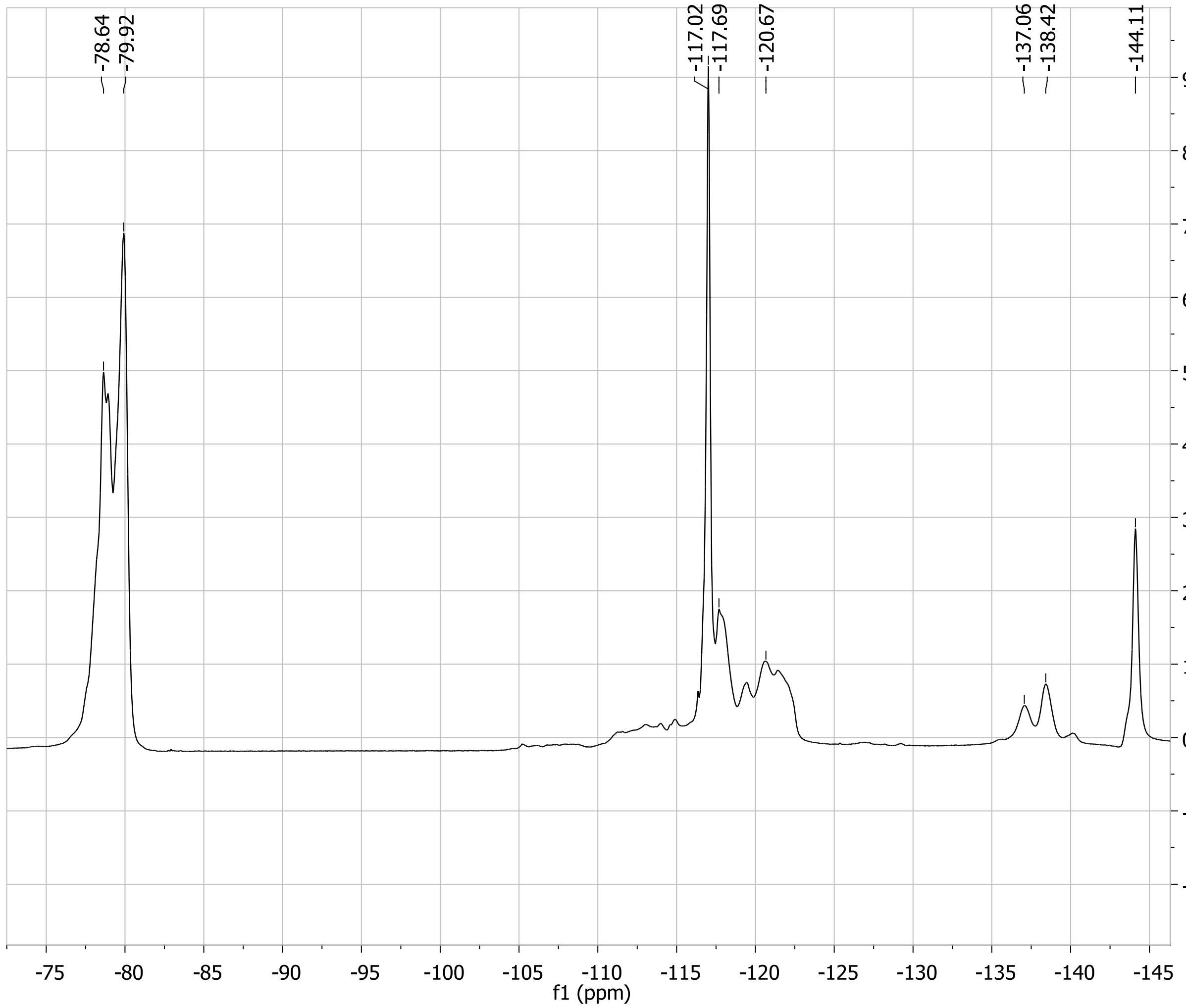

Figure 2.16. ^{19}F NMR spectrum of UAXE4A1 dissolved in acetonitrile-d3.

as in UAXR16. Based on the ^{19}F NMR spectrum showing four different peaks, it may be expected that little bulk TFE is present and the polymer consists mostly of bulk PSEPVE and PSEPVE monomers separated by one TFE monomer. An alternating structure would give two equivalent CF_2 groups vicinal to the side chain, with a nonequivalent CF_2 group between these. The fourth peak could be expected from the sequential addition of two PSEPVE monomers to give a CF_2 between two side chains from the PSEPVE.

Preparation of a soluble sulfonamide resin opens up the possibility to prepare sulfonimide polymers by post-treatment of the resin, as opposed to the current literature approach of polymerizing a sulfonimide monomer. Post-treatment production of sulfonimides gives an advantage that polymers can be prepared through solution polymerization as well as allowing preparation of polymers with multiple acid sites per side group. Multiple acid side chain monomers are difficult to polymerize, so preparation through the sulfonamide route should prove beneficial.[31] Preparation of these kinds of materials through this route has recently been reported by the 3M Company yielding water insoluble, low EW materials that show good fuel cell performances.[15]

2.3.4 MALDI-TOF MS Analysis

The only MALDI-TOF MS data on these types of materials available in the literature shows commercial Nafion® 1100 giving peaks with a spacing of 444 m/z in the MALDI spectrum up to weights of 3078 m/z.[32] Since Nafion® is considered to have a molecular weight of approximately 100,000 g/mol as well as a molar ratio of 6 TFE monomers per PSEPVE, the fact that no TFE is seen in the spectrum shows these measurements obviously are not giving an accurate representation of the material. Most samples prepared on this project do not give signals, likely due to the higher molecular weights or the increased crystallinity making it difficult for the polymer chains to fly through the time of flight detector. While proteins can be detected with molecular weights up to 1,000,000 g/mol,[33] synthetic chemists cannot produce materials with as narrow a PDI as nature. This increased PDI for synthetic polymers results in much lower signal to noise as many different (hundreds to thousands for a high PDI sample) chains with slightly different molecular weights are seen as opposed to polymers with a single molecular weight. To the author's knowledge, there are no MALDI-TOF spectrums for Nafion® type polymers above 3,000 g/mol in the literature.

However, UAXE4 is of sufficiently low EW and molecular weight that peaks can be seen up to approximately 4500 m/z, as shown in Figures 2.17. These peaks show repeat units of 100 and 443 m/z, corresponding to TFE and PSEPVE monomers, respectively, as shown in Figure 2.18. In the range of 2000 - 2500 m/z, polymer chains with 4-5 PSEPVE units and 0-4 TFE units can be seen. However, NMR and IR measurements show the EW to be closer to 600 g/mol, or an average of 1.5 TFE monomers per PSEPVE. As higher TFE content chains typically have higher molecular weights, it is possible that the MALDI is mass discriminating towards the lower molecular weight samples and is not showing the higher molecular weight polymer chains with higher TFE contents. Alternatively, it could be the higher TFE content chains are more crystalline and more difficult to vaporize by MALDI. Either way, it appears MALDI discriminates the higher EW samples from the lower EW samples.

2.3.5 Thermal Analysis of Copolymers

Thermal decomposition temperatures of several different equivalent weight samples are analyzed by TGA. As shown in Figure 2.19, high EW samples prepared at The University of Alabama show similar thermal stabilities to Nafion® 1100, with the 5% weight loss for samples UAXR8 and UAXR10 of 402 and 399 ˚C, only 5 and 8 ˚C lower than Nafion® 1100. A general

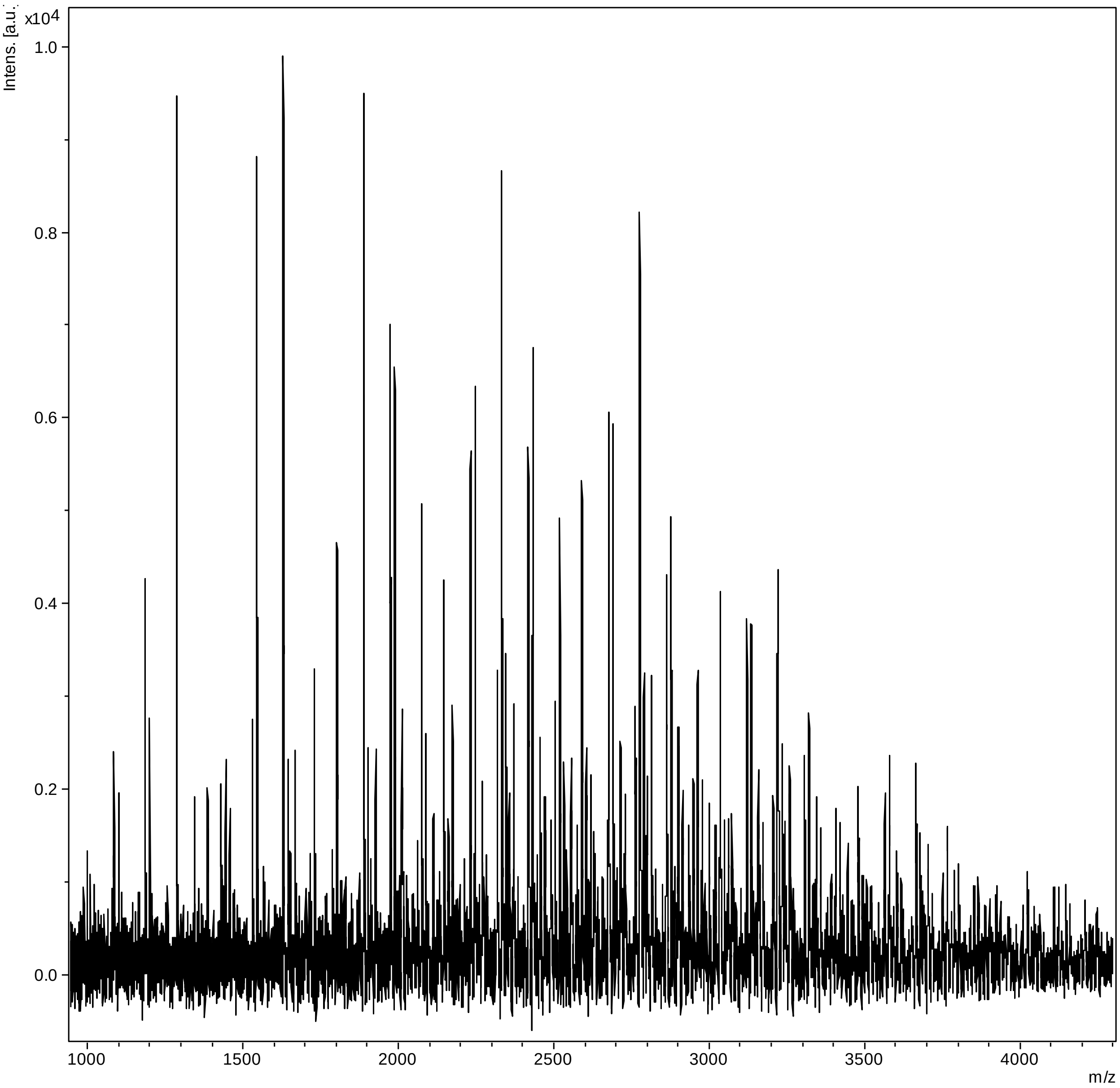

Figure 2.17. MALDI-TOF mass spectrum of UAXE4.

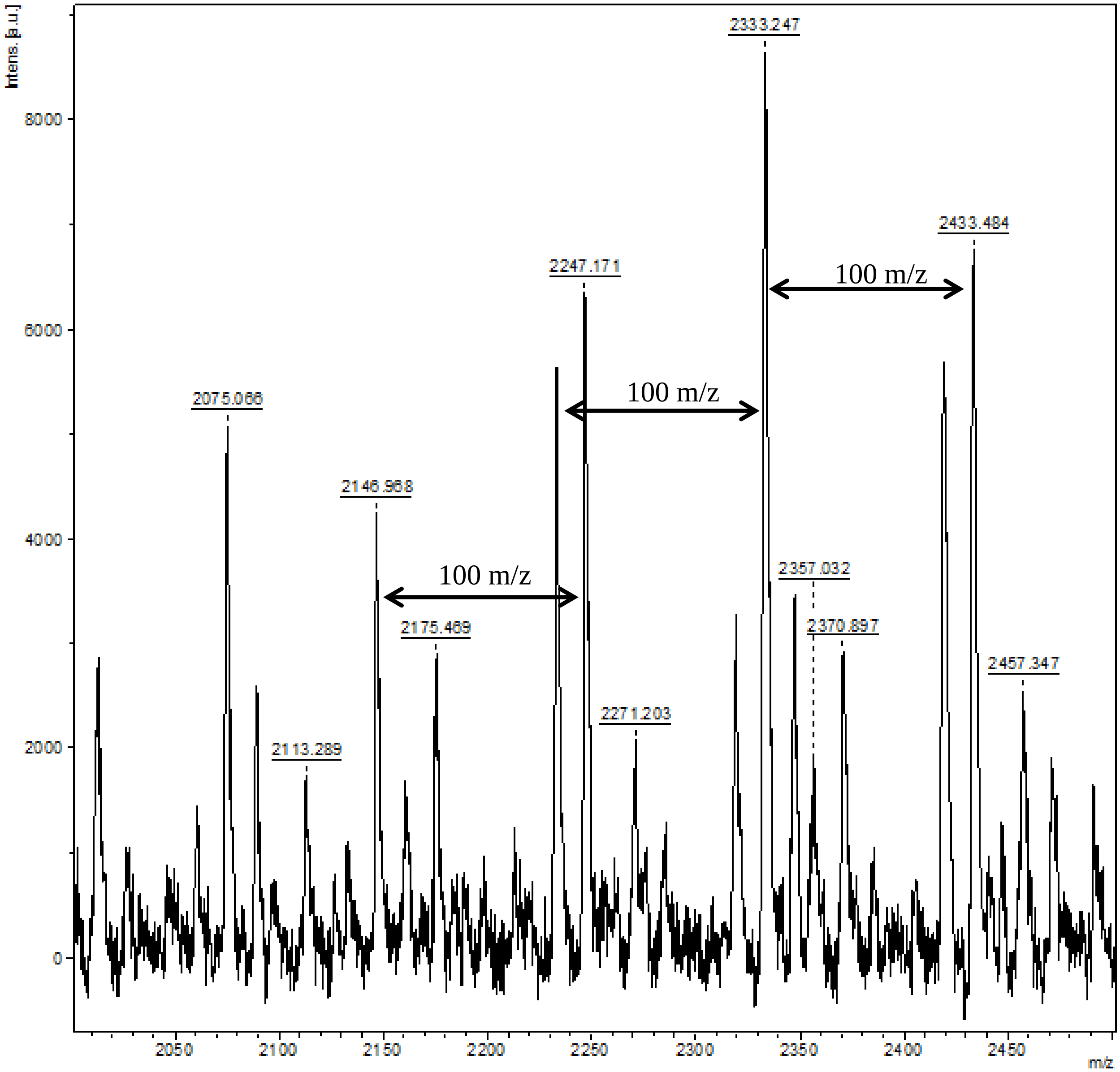

Figure 2.18. Expansion of MALDI-TOF mass spectrum of UAXE4.

decrease in thermal stability is seen with samples having lower ratios of TFE, which may account for this slightly lower thermal stability for the 900 - 1000 g/mol EW samples prepared here compared to Nafion® with an EW of 1100 g/mol. For example, sample the plot of the TGA data for sample UAXR16 with an EW of 550 g/mol can be seen in Figure 2.20, with a 5% T_d of 372 ˚C. This trend of lower thermal stabilities for lower EW materials may be caused by a decrease in molecular weights, less stable end groups, a higher degree of the less thermally stable PSEPVE side chains, or a combination thereof. While all the samples show thermal stabilities above 350 ˚C, much higher than the operating temperature of a fuel cell, spot heating can occur from membrane shorting in the cell. During preparation of the MEA, deformation of small areas of the membrane can occur. These thinner areas allow higher electron current to flow through the membrane, causing extreme temperatures in these localized areas, possibly leading to decomposition and stack failure over time. Higher thermal stabilities help to prevent membrane shorting from thermally decomposing parts of the membrane and destroying the entire fuel cell stack.

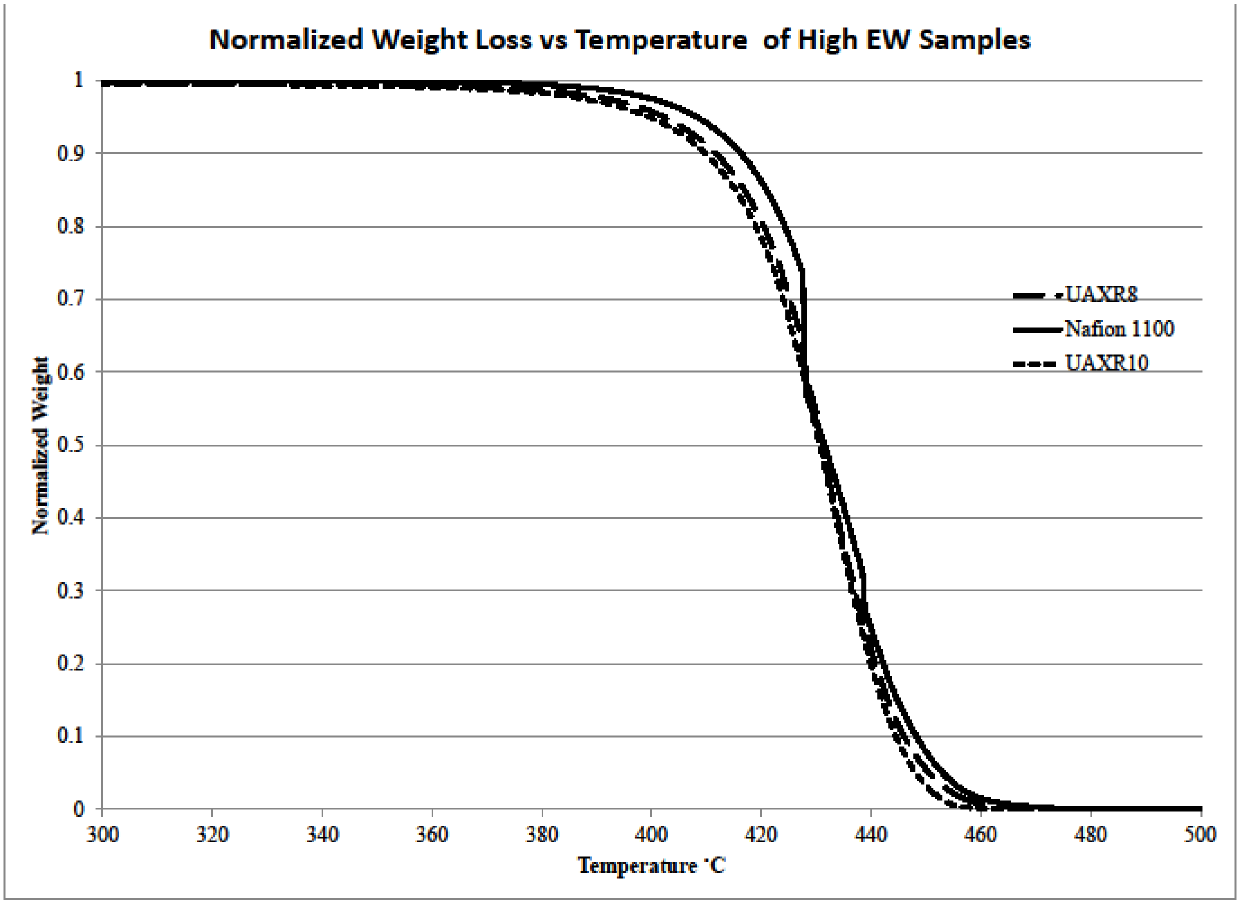

Figure 2.19. Thermal gravimetric analyses of high EW samples.

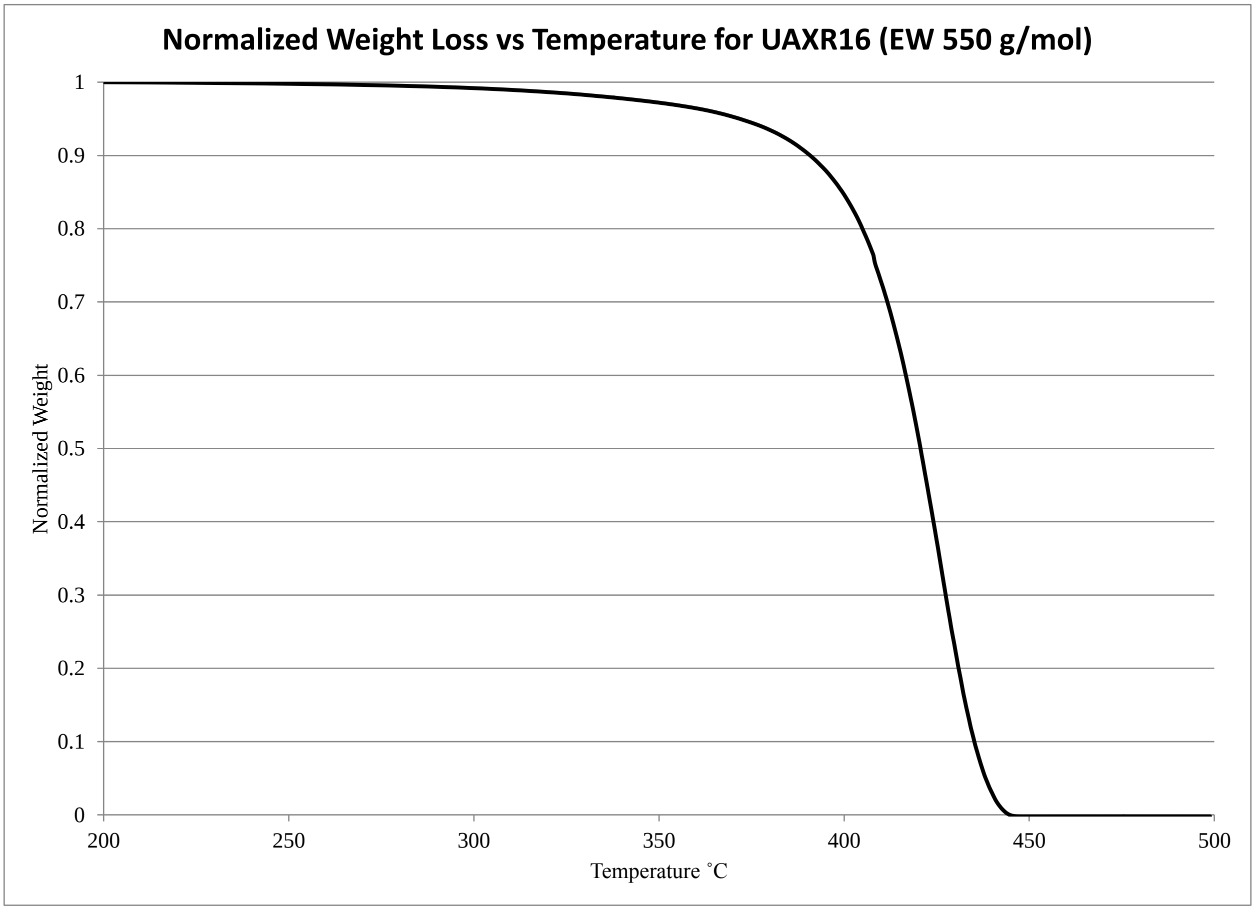

Figure 2.20. Thermal gravimetric analysis of UAXR16.

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CHAPTER 3

PREPARATION AND ANALYSIS OF PSEPVE AND DOW HOMOPOLYMERS

3.1 Introduction to poly(PSEPVE)

One of the original patents on copolymerizing PSEPVE with TFE also gives an example of the preparation of poly(PSEPVE).[1] However, no characterization was performed and the extent of work disclosed consists of only two sentences, raising concerns on whether the material was actually prepared or simply claimed to increase the company's patent position:

> "About 0.5 g of perfluoro[2(2-fluorosulfonylethoxy)propyl vinyl ether] is placed in a quartz tube which is then evacuated and sealed. After 24 hours irradiation with a mercury lamp, a clear viscous homopolymer is obtained."[1]

Despite this claim and example from 1966, peer-reviewed journal articles exist from as recently as 2007 that claim the homopolymer of PSEPVE cannot be prepared under radical conditions.[2] Additionally, as recently as the January 2011 Winter Fluorine Conference, top fluorine chemists have had discussions with the author and co-workers commenting that such a material cannot be prepared.[3] The difficulty in preparing the homopolymer arises from the large, bulky side chain that makes the kinetics of adding multiple PSEPVE monomers very slow due to steric effects. This can be seen with the reactivity ratios of PSEPVE with other monomers, where the reactivity ratio for PSEPVE is always well below 1.[2,4] However, despite these recent claims that poly(PSEPVE) cannot be prepared, two new reports of this homopolymer have appeared during the course of this project, while the material was also being prepared here.[5]

A patent application from Hsu *et al.* shows that a bulk polymerization of PSEPVE using hexafluoropropylene oxide dimer peroxide (HFPOdp) as the free radical initiator dissolved in HFC-4310 can produce poly(PSEPVE). Over the course of the 32 day polymerization a total of

4.284 mmol of HFPOdp is added to 340 g of PSEPVE in small aliquots every 2-3 days to yield 83.68 g of homopolymer in 24.6% yield. Thermal analysis shows "rapid weight loss starting about 300 ˚C" and a glass transition of 6.4 ˚C by DSC.[5a] Size exclusion chromatography (SEC) shows a number average molecular weight of 4300 g/mol and a weight average molecular weight of 9900 g/mol versus polystyrene standards of narrow molecular weight distribution. The number average molecular weight is the simple mean of the weights of the individual polymer chains, where the weight of all the polymer chains is added and then divided by the number of chains. Weight average molecular weights skew the data towards the higher molecular weight chains as some properties of polymers are more affected by these large chains than the shorter chains. The weight average molecular weight is calculated by the equation below where N_i corresponds to the number of chains with weight M_i.

$$M_W = \frac{\sum_{i=0}^{\infty} N_i M_i^2}{\sum_{j=0}^{\infty} N_j M_j}$$

Even more recently, a 2011 paper by Zhang *et al.* shows the preparation of poly(PSEPVE) using supercritical carbon dioxide as a solvent with a four-hour reaction time, giving 2.1% yield of poly(PSEPVE). No glass transition temperatures are measured, but the material is described as a liquid at room temperature and thermal gravimetric analysis shows 5% weight loss by approximately 270 ˚C. The polymer again shows low molecular weights with a number average of 4000 g/mol and a weight average of 10,700 g/mol by size exclusion chromatography (SEC) verse polystyrene standards of narrow molecular weight distribution.[5b]

The results from both of these groups show many similarities in the homopolymer produced. Low number average molecular weights are seen by SEC, with a number average below nine monomers per chain. High polydispersity indexes (PDI), the ratio of the weighted average molecular weight to the number average molecular weight, of 2.30 and 2.67 are seen by

Hsu and Zhang, respectively. The PDI of a polymer gives an idea of how broad or narrow the molecular weight distribution is, with a value of one occurring for polymers with a single molecular weight and numbers much above one occurring for polymers with a broad molecular weight distribution. The low yields seen are due to these low molecular weights producing small amounts of polymer.[5]

The materials show lower thermal stabilities than high EW copolymers of PSEPVE and TFE, such as Nafion® 1100 or sample UAXR10, which can be seen in Figure 2.18. As evidenced by the literature reactivity ratios for solution polymerizations of PSEPVE with TFE of 0.04 and 0.079, PSEPVE in a polymer chain strongly prefers the subsequent addition of TFE monomer to another PSEPVE monomer, due to the sterically bulky side chain on PSEPVE.[4,5b] Thus, the homopolymerization of PSEPVE proceeds slowly, at least partially explaining the low molecular weights and yields. Additionally, the reduced decomposition temperatures may be due to the reduced molecular weights and increased number of less thermally stable end groups.[6]

The literature reports of poly(PSEPVE) that have been published during this project show materials with both low molecular weights and low thermal stabilities. Better synthetic preparations need to be discovered in order to produce materials with higher molecular weights such that actual polymers are produced instead of low molecular weight oligomers. Alternatively, if high molecular weight polymers cannot be prepared, analysis should be done on the polymerization conditions to determine the reasons only oligomers are produced.

The nomenclature used for the polymers described throughout this Chapter is University of Alabama eXperimental Homopolymer (UAXH) followed by the sample number. Preparation of the sulfonamide resin gets the nomenclature UAXH1A2, where the number 1 is the polymer number based on the polymerization, A is signifying that the initial sulfonyl fluoride resin has been converted to the sulfonamide, and the number 2 refers to the specific preparation of the sulfonamide resin. The Dow homopolymer is signified UAXDH for University of Alabama eXperimental Dow Homopolymer.

3.2 Experimental

See Table 3.1 (vide infra) for full list of poly(PSEPVE) polymerizations.

3.2.1 Mercury Lamp Initiated Homopolymerization UAXH6

Repeating Example 6 from U.S. Patent 3,282,875, 30.70 g of degassed PSEPVE is added into a 2.2 cm outer diameter sealed quartz vessel.[1] Irradiation is performed using a low-pressure mercury lamp inside a mirrored reactor vessel with fan cooling to keep the reaction temperature at 35 ˚C. After seven days irradiation, the volatile products are removed on a vacuum line at 50 mtorr heating up to 150 ˚C to yield 1.14 g of polymer in 3.71% yield.

3.2.2 254 nm Rayonet Initiated Homopolymerization UAXH7

Inside a 2.2 cm outer diameter sealed quartz tube is placed 46.46 g of degassed PSEPVE. The quartz tube is placed inside a Rayonet reactor containing low-pressure mercury lamps and fan cooling, and the entire reaction system is placed inside a cold room at 5 ˚C. After six days irradiation, the volatile products are removed on a vacuum line at 50 mtorr heating up to 150 ˚C to yield 1.94 g of polymer in 4.18% yield.

3.2.3 UV Initiated Decomposition of Diacyl Peroxides to Initiate UAXH8

Inside a sealed quartz tube with an outer diameter of 2.2 cm is placed 59.61 g of degassed PSEPVE. The quartz tube is placed inside a Rayonet reactor containing low pressure mercury lamps and fan cooling, and the entire reaction system is placed inside a cold room at 5 ˚C. With irradiation turned on, a 0.3 mL aliquot of 0.106 M 3P in perfluorohexane is added on days 1, 2, 3, 8, 9, and 11. After workup, 4.90 g of polymer is obtained in 8.22% yield.

3.2.4 3P Initiated Hompolymerization UAXH2 at 20 ˚C

Inside a glass apparatus containing a septum to add initiator aliquots and a 3-way valve connected to a vacuum source, to degas the monomer, and house nitrogen, to keep a nitrogen pad on the system, is added 124.25 g of PSEPVE. Every five days to this mixture is added 2.4 mL of a 0.164 M solution of 3P in HFC-4310, giving a molar concentration of 3P in the reaction of 5.39 mM. After five additions of initiator, the volatile co-products are removed yielding 35.12 g of polymer in 28% yield.

$\{CF_2^aCF^b[OCF_2^cCF^d(CF_3^e)OCF_2^fCF_2^gSO_2F^h]\}_n$ ^{19}F NMR Spectrum of UAXH2 recorded in R113:: δ^a -105 - -118 (broad); δ^b -138.8 (1F, broad); δ^c -82.1 (4F); δ^d -146.2 (1F); δ^e -81.1 (3F); δ^f -82.1 (4F); δ^g -114.4 (2F); δ^h 42.3 (1F).

ATR-FTIR Analysis (cm^{-1}): 1465 (s); 1314 (w); 1237 (s); 1188 (s); 1131 (s); 983 (s); 821, 798 (doublet, m).

3.2.5 High Concentration of 3P Initiated Homopolymerization UAXH5 at 20 ˚C

To an FEP reactor as seen in Figure 3.1 is added 173.43 g of deoxygenated PSEPVE. Every two days to this mixture is added 10.0 mL of a 0.106 M solution of 3P in perfluorohexane, giving a molar ratio of PSEPVE to 3P per addition of 180 : 1. Initiator additions are performed by connecting the reactor vessel valve to a low pressure nitrogen source and keeping a constant stream of nitrogen flowing out of the vessel when the top plug is removed. The initiator storage container is attached to a high pressure nitrogen source and a nitrogen pad is maintained while the container is open. A syringe is used to draw up initiator from the initiator storage container and added to the reaction vessel. After three additions of initiator, the volatile products are removed at 150 ˚C and 50 mtorr yielding 28.7 g of polymer in 16.6% yield.

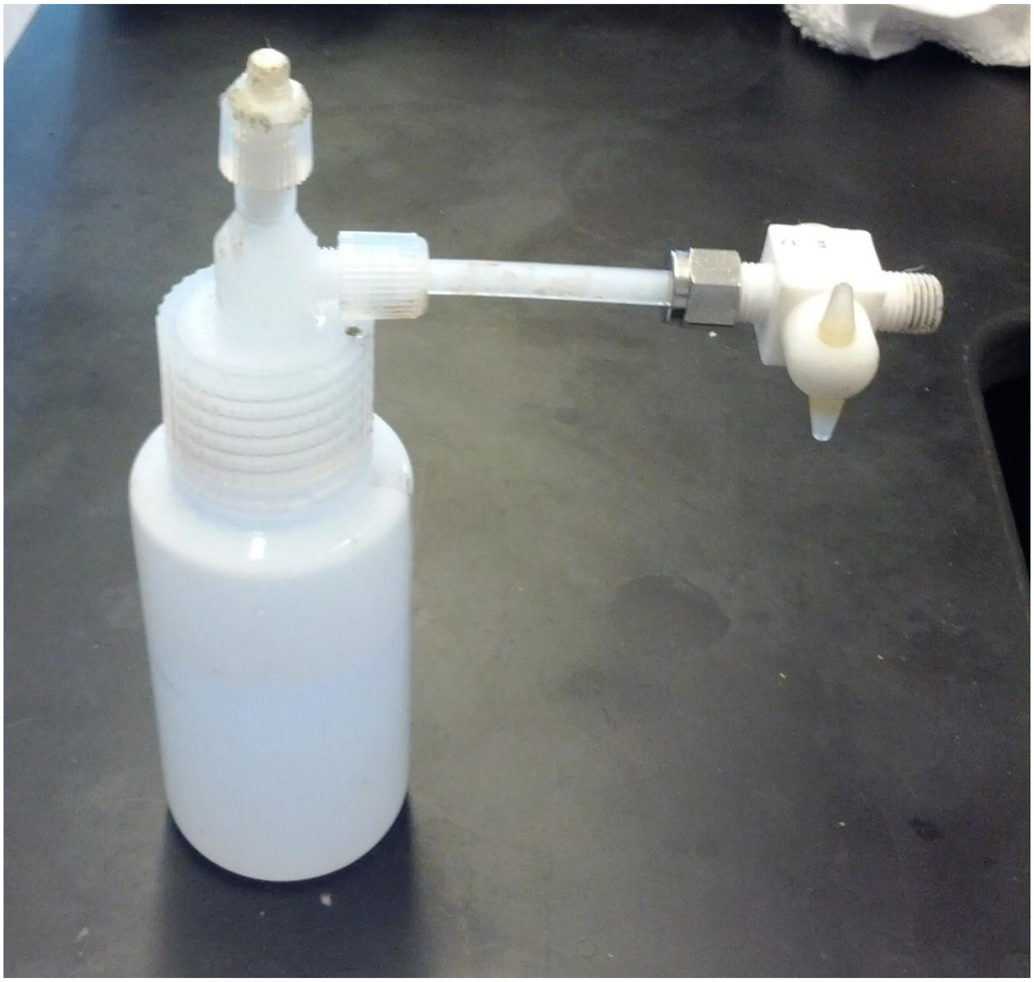

Figure 3.1. FEP polymerization vessel.

3.2.6 Low Concentration of 3P Initiated Homopolymerization UAXH3 at 20 ˚C

Inside the aforementioned FEP reactor is added 174.19 g of deoxygenated PSEPVE. Every 24 hours to this mixture is added 1.0 mL of a 0.106 M solution of 3P in perfluorohexane, giving a molar ratio of PSEPVE to 3P per addition of 4000 : 1. Five additions of initiator were performed, before which a roughly 1.0 mL aliquot is taken to calculate the weight% solids, as seen in Figure 3.2. After a reaction time of seven days, the volatile products are removed yielding 20.21 g of polymer in 12.8% yield.

$\{CF_2^aCF^b[OCF_2^cCF^d(CF_3^e)OCF_2^fCF_2^gSO_2F^H]\}_n$ ^{19}F NMR spectrum of UAXH3 recorded in R113 (see Figure 3.3): δ^a -105 to -118 (broad), δ^b -138.8 (broad), δ^c -81.1, δ^d -143.6 (1F), δ^e -82.1 (7F), δ^f -81.1, δ^g -114.4, δ^h 47.1.

ATR-FTIR Analysis (cm^{-1}): 1314 (w); 1235 (s); 1183 (s); 1136 (s); 1058 (m); 981, 971 (doublet, m).

3.2.7 Low Concentration of 3P Initiated Homopolymerization UAXH4 at 50 ˚C

To the aforementioned FEP reactor is added 176.45 g of deoxygenated PSEPVE placed in a 50 ˚C Krytox® bath. Every three hours to the mixture is added 1.0 mL of a 0.106 M solution of 3P in perfluorohexane, giving a molar ratio of PSEPVE to 3P per addition of 3700 : 1. After six initiator additions, the volatiles are removed yielding 16.94 g of polymer in 9.60% yield.

3.2.8 Low Concentration of HFPOdp Initiated Homopolymerization UAXH11 at 5 ˚C

The aforementioned FEP vessel containing 230.97 g of deoxygenated PSEPVE is placed inside a desiccator under nitrogen atmosphere, and the entire system is placed inside a cold room at 5 ˚C. Every 24 hours to this mixture is added 0.8 mL of a 0.160 M solution of HFPOdp in perfluorohexane, giving a molar ratio of PSEPVE to HFPOdp per addition of 4000 : 1. After six additions of initiator, volatile products are removed yielding 13.85 g of UAXH11 in 6.00% yield.

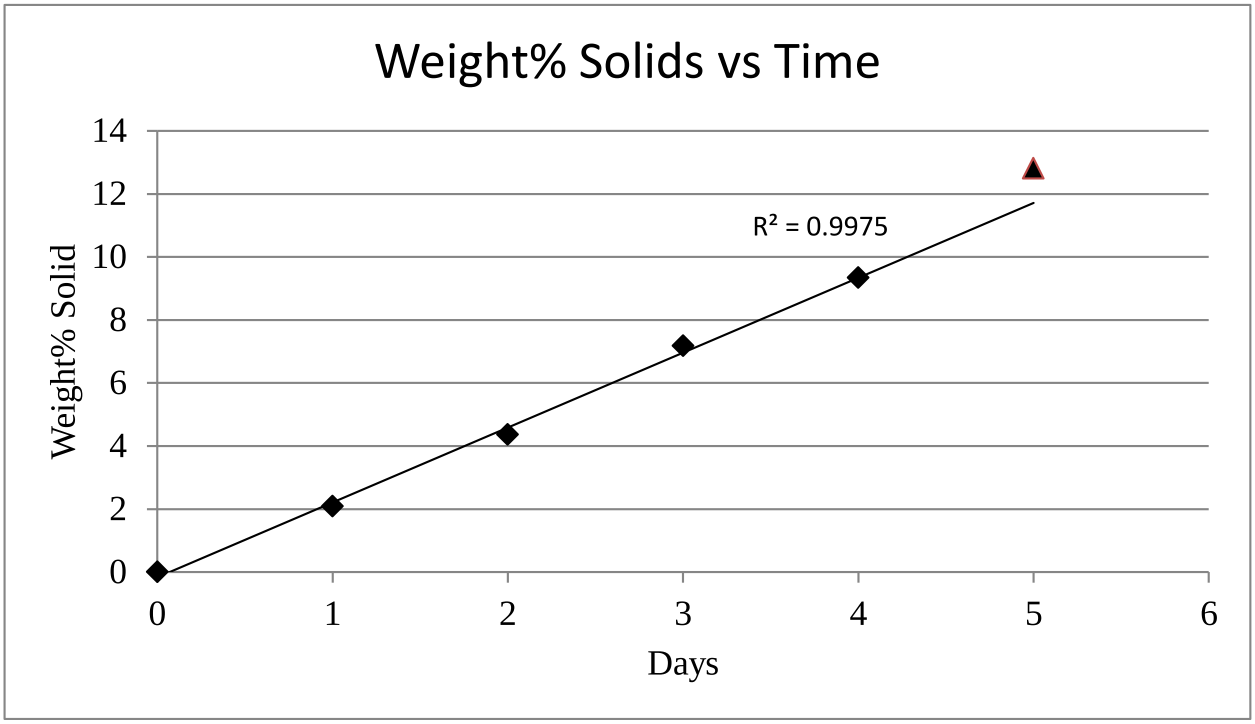

Figure 3.2. Weight percent solids vs. time during UAXH3 polymerization.

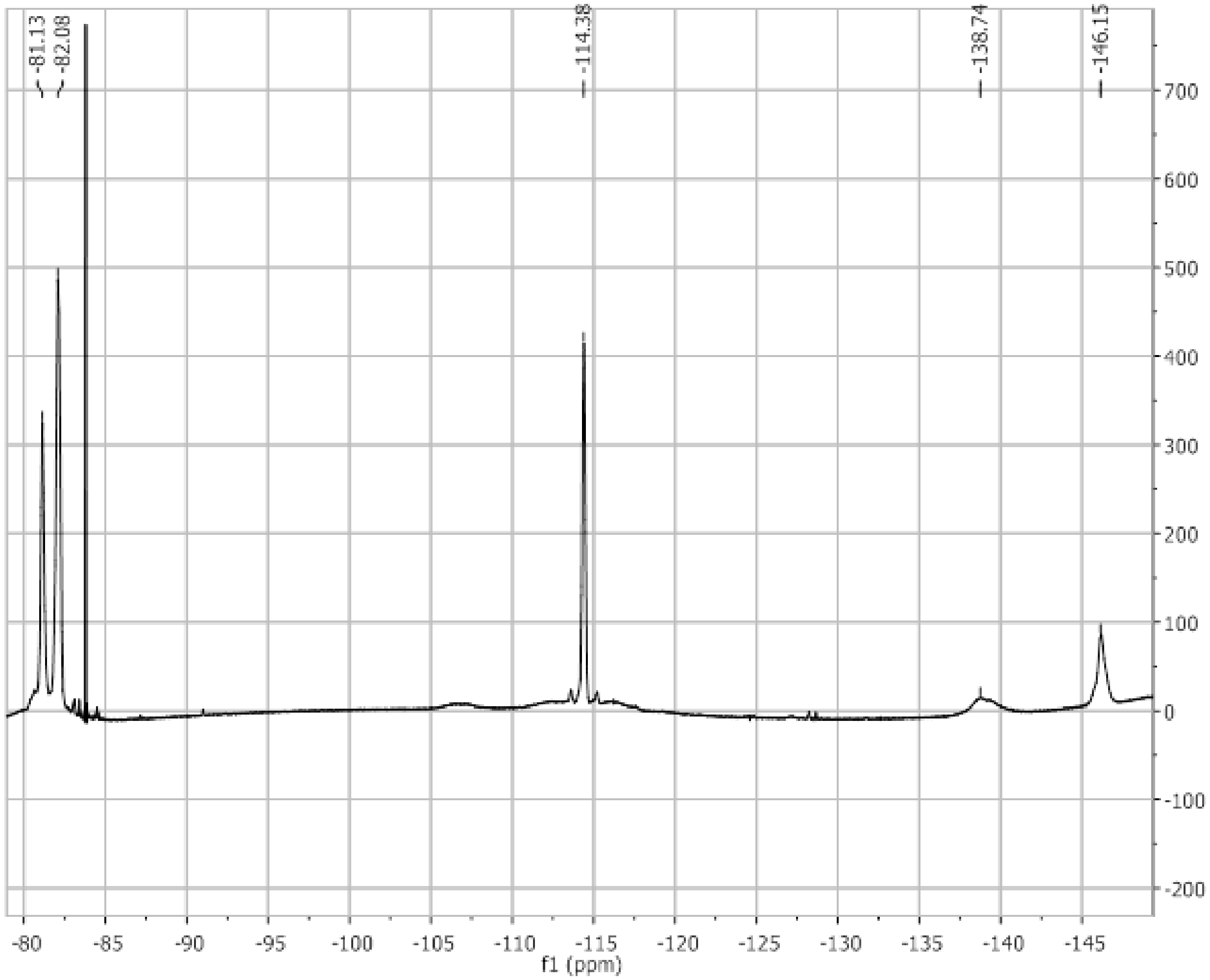

Figure 3.3. ^{19}F NMR spectrum of UAXH3 sulfonyl fluoride resin dissolved in R113.

3.2.9 3P Initiated Hompolymerization UAXDH1 at 20 ˚C

Inside the FEP reactor vessel is added 140 g of deoxygenated Dow vinyl ether. Every five days to this mixture is added 4.4 mL of a 0.164 M solution of 3P in HFC-4310, giving a molar ratio of Dow to 3P per addition of 710 : 1. After five initiator additions, the volatile co-products are removed yielding 39 g of polymer in 28% yield.

ATR-FTIR of UAXDH1 (see Figure 3.4) (cm^{-1}): 1464 (s); 1325 (w); 1243 (w); 1175 (s); 1139 (s); 999 (s); 819 (m); 800 (m).

3.2.10 Amidation of Homopolymer Samples

Amidation of the homopolymers is performed similarly to Example 2.2.14 by first taking a heat gun to the polymer inside a round-bottomed flask and spinning the flask to coat the polymer along the interior surface of the flask to increase its surface area. Workup is performed by dissolving the sample in diethyl ether and extracting the ammonium fluoride byproduct with water. By placing the polymer in a vacuum desiccator at 120 ˚C and 100 torr overnight the material is dried to less than 10 ppm H_2O content according to Karl Fischer titrations.

$\{CF_2^a CF^b [OCF_2^c CF^d (CF_3^e) OCF_2^f CF_2^g SO_2NH_2]\}_n$ ^{19}F NMR spectrum of UAXH3A1 in DMSO-d6 at 330 K (see Figure 3.5): δ^a -105 to -118 (broad), δ^b -138.9 (1F, broad), δ^c -82.0 (4F), δ^d -146.3 (1F), δ^e -80.7 (3F), δ^f -82.0 (4F), δ^g -119.0, $\delta^{CF2SO3H}$ -117.6.

ATR-FTIR of UAXH3 base resin (see Figure 3.6) (cm^{-1}): 1465 (s); 1306 (w); 1237 (s); 1175 (s); 1131 (s); 983 (s); 820 (m); 798 (m).

ATR-FTIR Analysis of UAXH3A1 (see Figure 3.7) (cm^{-1}): 1387 (m); 1314 (w); 1236 (s); 1175 (s); 1127 (s); 981 (s); 922 (m).

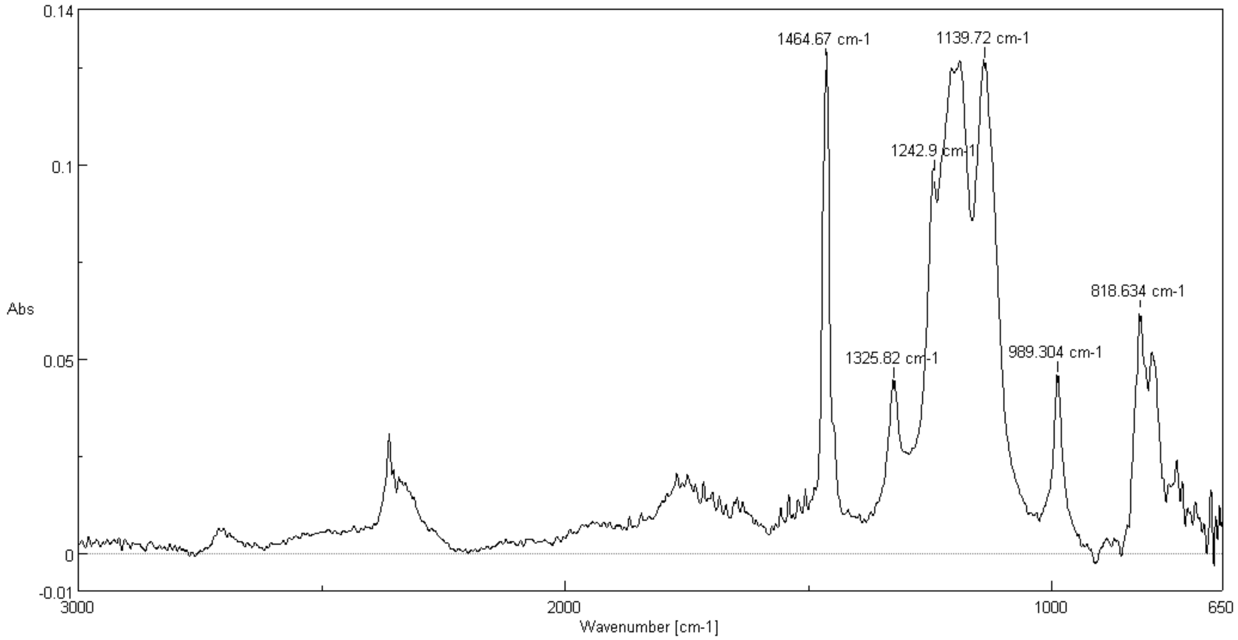

Figure 3.4. UAXDH1 ATR-FTIR spectrum.

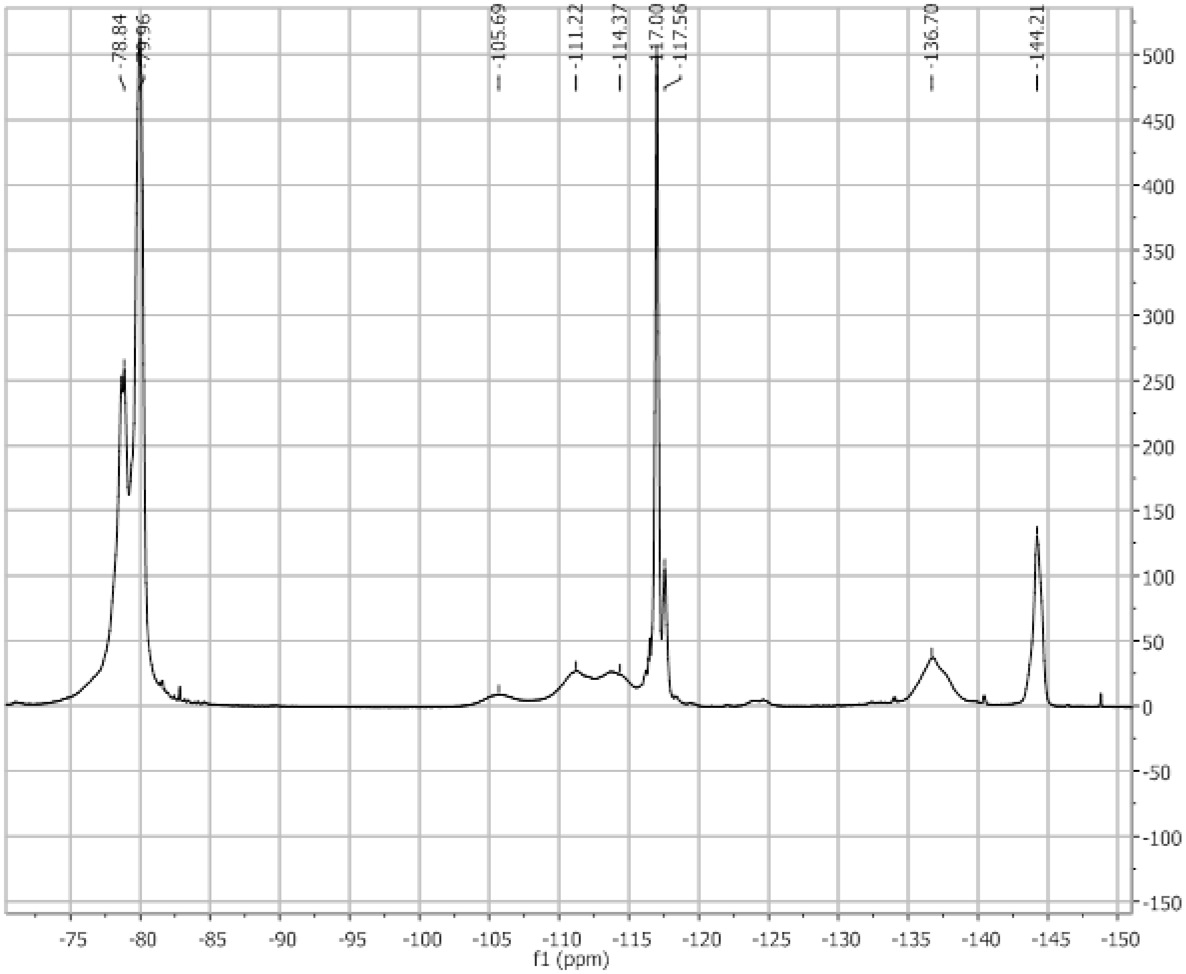

Figure 3.5. ^{19}F NMR spectrum of UAXH3A1 dissolved in DMSO-d6 at 332 K.

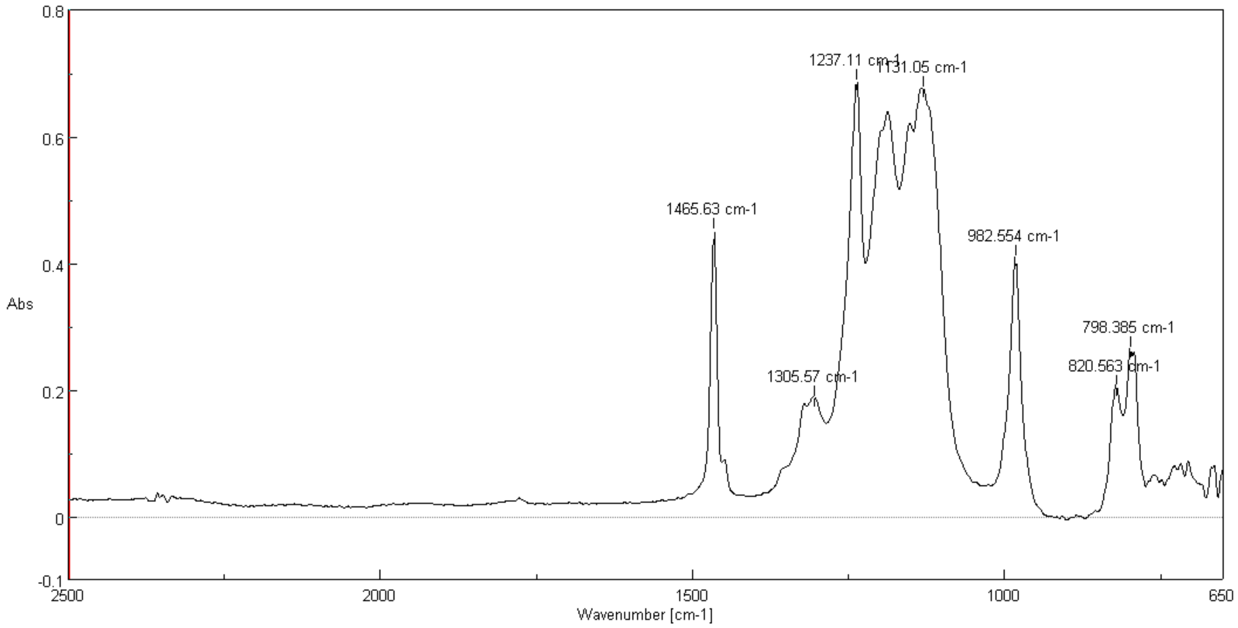

Figure 3.6. UAXH3 ATR-FTIR spectrum.

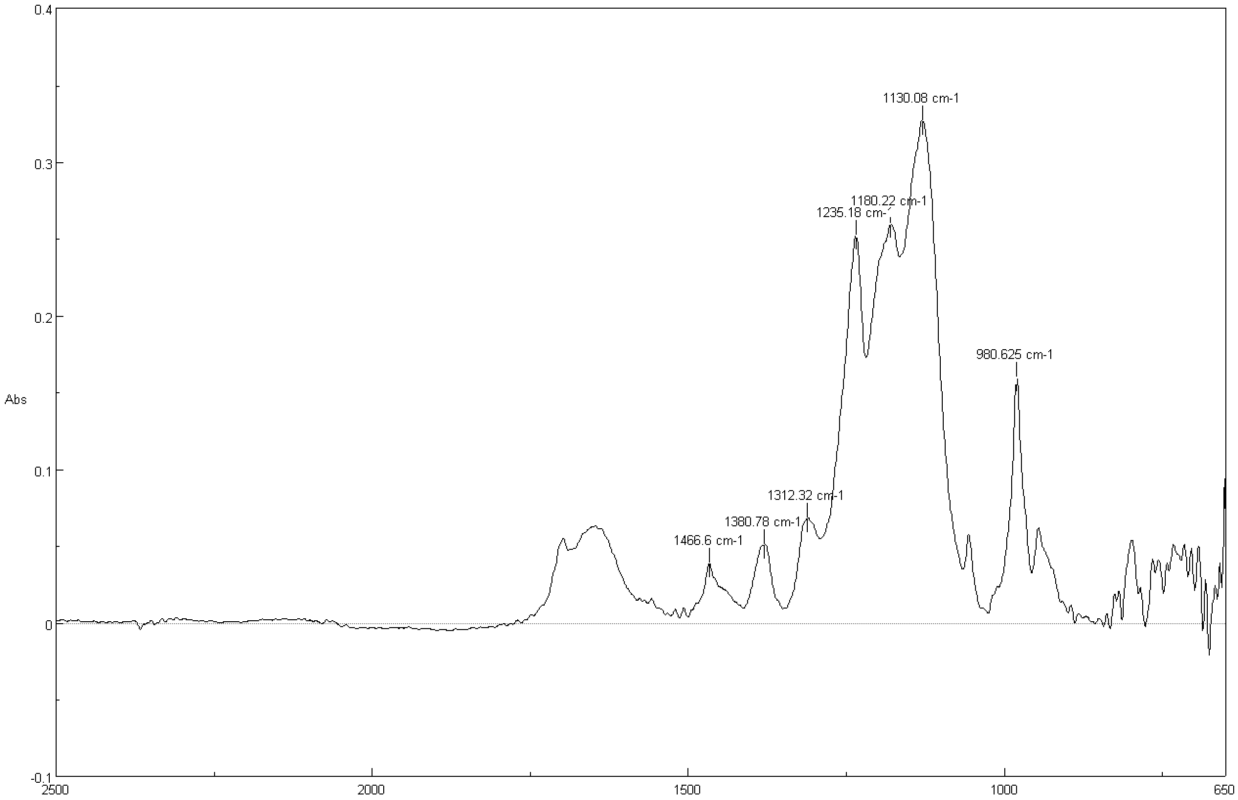

Figure 3.7. UAXH3A1 ATR-FTIR spectrum.

3.2.11 Hydrolysis of Homopolymer Samples

Hydrolysis of homopolymers is performed using excess 14 M ammonium hydroxide at 50 ˚C until the entire polymer sample is dissolved. The excess ammonium hydroxide and water are removed by heating up to 120 ˚C overnight at 100 torr, which also removes ammonium fluoride that is not trapped in the polymer matrix by sublimation.

$\{CF_2^aCF^b[OCF_2^cCF^d(CF_3^e)OCF_2^fCF_2^gSO_3H]\}_n$ ^{19}F NMR spectrum recorded in D_2O/DMSO-d6 at 330 K (see Figure 3.8): δ^a -105 to -118 (broad), δ^b -136.2 (1F, broad), δ^c -80.1 (7F), δ^d -143.6 (1F), δ^e -80.1 (7F), δ^f -80.1 (7F), δ^g -119.0.

ATR-FTIR Analysis (cm^{-1}): 1314 (w); 1235 (s); 1183 (s); 1136 (s); 1058 (m); 981, 971 (doublet, m)

3.2.12 MALDI-TOF MS Analysis

Analysis of the sulfonamide resins by MALDI-TOF mass spectrometry is performed using a Bruker Ultraflex TOF instrument by dissolving 20 mg of resin in 1 mL acetonitrile. An aliquot of 10 microliters of this solution is mixed with 100 microliters of a solution of 7.5 mg/mL 2,5-dihydroxybenzoic acid (DHB) in a 50:50 acetonitrile : water (v/v) containing 0.1 wt% trifluoroacetic acid (TFA). Onto a stainless steel plate is spotted 30 microliters of this final solution, which is allowed to dry before analysis. Analysis of the ammonium sulfonate resins by MALDI-TOF MS is performed similarly except the matrix solution contains only water with no acetonitrile.

3.2.13 Thermal Analysis (TGA and DSC)

Differential scanning calorimetry (DSC) measurements were performed using approximately 10 mg of polymer sample in an aluminum pan. Using a TA Instruments Q200 instrument, the samples were quickly heated to 200 ˚C and allowed to anneal for 2 hours before

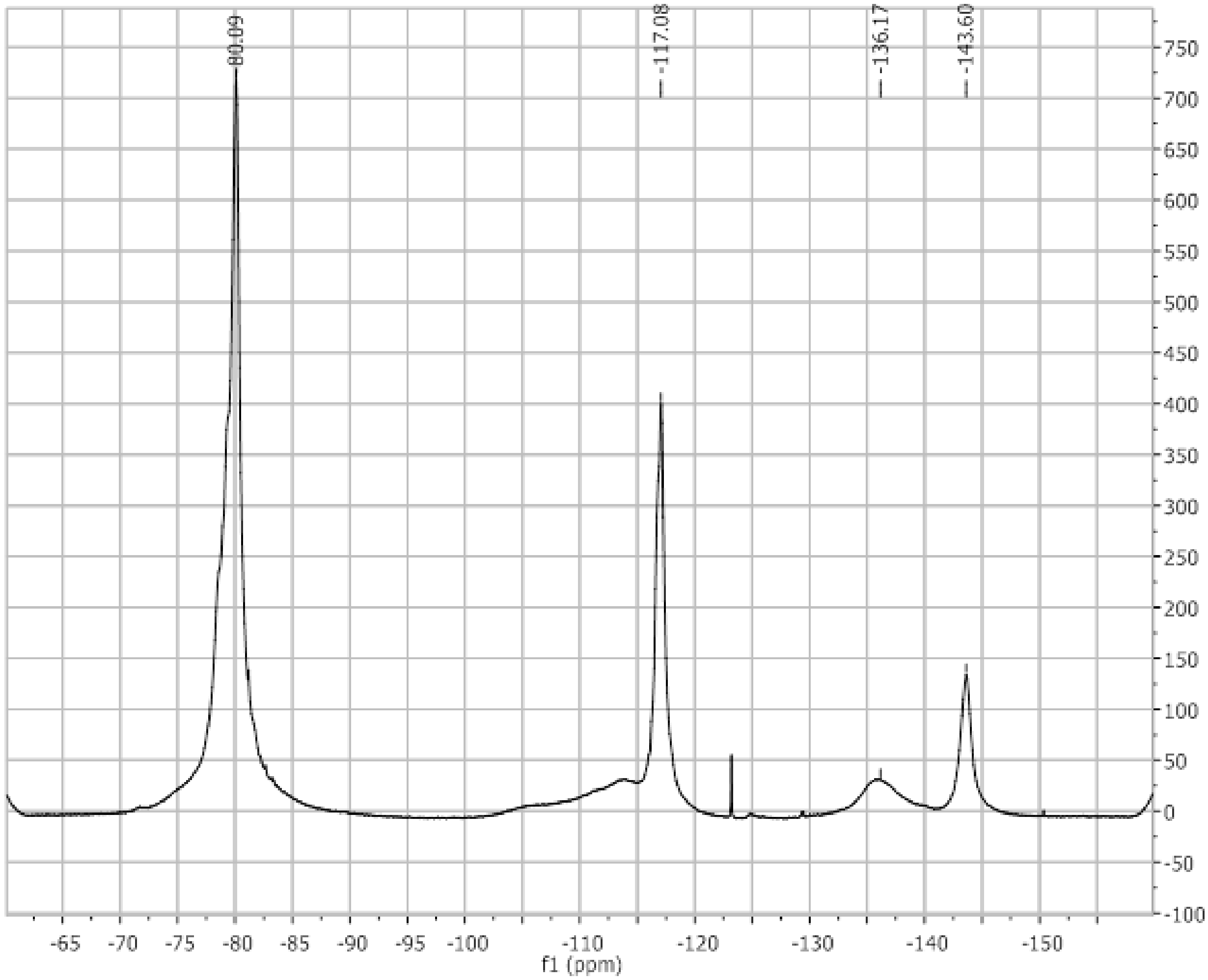

Figure 3.8. ^{19}F NMR spectrum of UAXH3H1 dissolved in mixture of DMSO-d6, D_2O, KOH at 332 K.

Table 3.1. Homopolymerizations of PSEPVE and Dow Vinyl Ethers.

Sample	Monomer (g)	Initiator per Addition (mmol)	Initiator Additions / Frequency	Initiator	Product (g)	5% Td ˚C	Tg ˚C
UAXH1	86	0.3	4 / Every 5 Days	3P in HFC4310	11.58	-----	-----
UAXH2	124.25	0.39	5 / Every 5 Days	3P in HFC4310	35.12	361	20.1
UAXH3	174.19	0.1	5 / Daily	3P in HFC4310	20	362	24.6
UAXH4	176.45	0.11 at 50 ˚C	6 / 3 Hours	3P in HFC4310	14	-----	6.9
UAXH5	173.43	1.1	3 / Every 2 Days	3P in C_6F_{14}	28.7	-----	16.7
UAXH6	30.7	Hg Lamp at 30 ˚C	7 Days	NONE	1.14	286	-----
UAXH7	46.46	Hg Lamp at 5 ˚C	7 Days	NONE	1.94	365	27.9
UAXH8	59.61	254 nm + 0.036 at 5 ˚C	6 / Daily	3P in C_6F_{14}	4.9	-----	17.5
UAXH10	193	0.11	6 / Daily	3P in C_6F_{14}	20.54	-----	-----
UAXH11	230.97	0.13 at 5 ˚C	5 / Daily	HFPOdp in C_6F_{14}	13.85	-----	23.1
UAXH12	84	0.016 at 5 ˚C	5 / Daily	HFPOdp in C_6F_{14}	3.43	-----	28.5
UAXH13	187	0.032 at 5 ˚C	9 / Daily	HFPOdp in C_6F_{14}	9.01	-----	-----
UAXH14	124	2.9	1	3P in C_6F_{14}	21.69	-----	-----
UAXDH1	140	0.71	5 / Every 5 Days	3P in HFC4310	39	373	44
UAXDH2	225	0.24	6 / Daily	3P in C_6F_{14}	20.86	-----	-----

cooling to -50 ˚C and reheating to 200 ˚C at a rate of 10 ˚C/min. Glass transition temperatures are reported as the midpoint of the thermal transition.

Thermal gravimetric analysis (TGA) is performed on approximately 30 mg samples in a platinum pan using a TA Instruments TGA 9250 under a nitrogen purge. Samples were heated to 120 ˚C and allowed to sit for 1 hour to remove any adventitious water, e.g., absorbed from the atmosphere, before heating to a final temperature of 600 ˚C at a rate of 5.0 ˚C/min.

3.3 Results and Discussion

3.3.1 Preparation of Homopolymers

Bulk polymerizations similar to Hsu *et al.* were employed with the main difference being shorter reaction times of 5-6 days as opposed to 32 days. Also, for the room temperature free-radical initiated polymerizations performed herein, the more thermally stable 3P initiator is used with a half-life at 25 ˚C of 16 hours,[7] compared to HFPOdp with a 1.9 hour half-life.[8] HFPOdp is used only for the 5 ˚C polymerization due to its lower thermal stability than 3P, which has almost no radical formation at 5 ˚C. The longer half-life of 3P reduces the radical flux in the polymerization in an attempt to increase molecular weight. Lowering the number of initiator additions should also have the effect of lowering polydispersity index (PDI).[9] To further increase molecular weight, perfluorohexane was used as the initiator solvent instead of HFC-4310. Removal of all hydrocarbons that are capable of chain transfer reactions reduces the rate of termination and can help increase molecular weight. An FEP reactor vessel is also used to eliminate the possibility of any surface termination mechanisms associated with glass. To prevent any oxygen from leaking into the FEP reactor vessel, which has an oxygen permeability of 11,600 $cm^3(m^{-2})(24\ h^{-1})(atm^{-1})$ for a 1 mil thick sample, the reactor vessel is stored under a nitrogen pressure of 200 torr and inside a desiccator flushed with nitrogen. The samples produced were similar in description to the homopolymer produced by Hsu, “a clear, brittle, somewhat tacky solid.”

Yields are low for the polymerizations due to the low molecular weights. While increasing the amount of initiator added into the polymerization will increase the yield, it will also result in lower molecular weight samples. High and low temperature reactions were also performed to test if yields could be increased through any of these routes. Both reaction conditions resulted in low yields as well. The high temperature reaction gives polymers with molecular weights that are very low, resulting in low yield, while the low temperature reaction slows the kinetics so much that even though the molecular weights are higher the yield is still low due to kinetics. Additionally, UV reactions were attempted to see if molecular weights or yields could be increased with this initiation mechanism, but these reactions were also without much success.

During the course of the 3P initiated polymerization UAXH3, aliquots of the polymerization were taken every 24 hours before the addition of initiator to measure the weight percent solids. These measurements are presented in Figure 2 showing a linear increase in the amount of polymer present in the reaction after each addition of initiator. If the slope of the line were exponentially increasing, then the input of initiator is faster than the decomposition to radicals, causing a gradual increase in the radical flux over the course of the polymerization and a high PDI. Workup began after waiting two days after the last initiator addition, and the weight percent solids is measured at 12.8%, above the slope of the graph that predicts the weight percent solid 24 hours after the previous initiator addition. This increased weight percent solids shows that 24 hours after an addition of initiator when the next aliquot is added, there still remains some unreacted initiator in the reaction from the previous addition. Thus, the concentration of initiator is approaching a steady-state value, although still not ideal.

To increase yields in the polymerizations, large aliquots of initiator can be added. In most polymerizations this would result in lower molecular weights of the polymer produced. However, since the molecular weights for the homopolymerization of PSEPVE depend so highly on the β-scission reaction (discussed more in Section 3.3.3) that is independent of the concentration of initiator, it may be possible to obtain similar molecular weights and higher yields of polymer by simply adding more initiator, as done in UAXH14. This route may also have the added benefit that the polymer produced could have more perfluoroethyl (3P) end groups than the less stable acid end groups. However, without instrumentation for carrying out SEC (or GPC) measurements, it is not possible to verify whether the molecular weights are similar with a corresponding increase in the concentration of initiator. Finding the ideal concentration of initiator to maximize yield and molecular weight while also reducing the number of acid-end-group terminated chains could prove promising future work if these homopolymers are ever commercialized or even tested in a fuel cell for lifetime studies.

Hydrolysis of the samples requires concentrated ammonium hydroxide at 50 ˚C overnight, where complete hydrolysis is verified by the polymer being dissolved in solution as well as the absence of a peak around 40 ppm in the ^{19}F NMR spectrum. Ammonium hydroxide is utilized as it allows for the excess base to be removed by distillation, unlike KOH or other alkali metal hydroxide bases. Acidification of the samples can be performed by dissolving in water, and running the sample through a Nafion® acid exchange column. However, as the material is highly soluble in water and hygroscopic, conductivity measurements and membrane preparation are quite difficult and could not be performed here.

3.3.2 Characterization of Homopolymers

Infrared measurements show similar stretches to those of the copolymers produced in Chapter 2 and commercial Nafion®. The biggest difference between the spectra for the copolymers and homopolymer is the increased absorbance at 1237 cm^{-1}. This peak likely corresponds to the CF_3 group pendent to the backbone of PSEPVE, as literature infrared spectra for triflic anhydride, trifluoroacetic anhydride, and 1,1,1,2,3,3,3-heptafluoro-2-iodopropane all show strong absorbances between 1238 and 1244 cm^{-1}.[10] The IR spectrum for the homopolymer of the Dow vinyl ether shows a weak stretch here despite not having any CF_3 groups in the monomer. This absorbance could be due to the CF_3 end groups from the 3P initiator. Alternatively, the peak could arise from a CF absorbance as PSEPVE contains two, one in the backbone of the polymer and one on the side chain, while Dow contains only the CF from the backbone. This interpretation may better explain the presence of the stretch in the poly(Dow) spectrum but its decreased intensity compared to poly(PSEPVE). Without an increased number of model compounds, it is difficult to say with certainty to what functional group the stretch corresponds. Careful measurement of EWs by titration and then correlating this data to the intensity of the absorbance at 1237 cm^{-1} may allow for a better determination of EW by IR for low equivalent weight materials. Similarly, correlation of the IR intensity of the absorbance at 1237 cm^{-1} for the Dow material to molecular weight data from size exclusion chromatography (SEC) may allow for molecular weight determination of poly(Dow) by IR spectroscopy, if the absorbance corresponds to the CF_3 from end groups.

^{19}F NMR spectroscopy is performed on the sulfonyl fluoride resin in 1,1,2-trichloro-1,2,2-trifluoroethane (R113), the sulfonamide resin in DMSO-d6 at 60 ˚C, and the hydrolyzed sulfonate in a 40:60 v/v mixture of DMSO-d6 and D_2O at 60 ˚C to increase resolution. Due in part to the samples being oligomers with high polydispersity indices, fine coupling cannot be obtained with any samples, and broad peaks are often observed due to the slightly different environment within the chain and possibly different intermolecular forces. High temperature NMR spectroscopy sharpens the peaks up somewhat, but several signals still do not give proper integration ratios due to their broadness, namely the peak at -139 ppm assigned to the methine fluorine on the backbone. The complete absence of vinyl fluorine peaks (normally seen at -117, -125, and -138 ppm in the monomer) in the spectrum of the sulfonyl fluoride resin in R-113 verifies the absence of any remaining unreacted monomer in the sample. The CF_2 group in the backbone of the polymer gives almost no sharp signal, likely due to restricted bond rotation by the bulky side chain, and is only observed as an extremely broad hump in the baseline between -110 and -120 ppm.

Thermal analysis of the samples is performed by TGA and DSC. Figures 3.9 and 3.10 show similar decomposition patterns for the Dow and PSEPVE homopolymers, with slow weight loss of approximately 5% of the sample's total mass upon heating up to 360 ˚C followed by rapid weight loss beginning around 370 ˚C. On the other hand, a comparison of the thermal decomposition of these samples to the literature reports shows an approximately 90 ˚C increase in the thermal decomposition temperature (usually considered the temperature where 5% of the sample's mass has been lost).[5b] As described below (*vide infra*), this increase in thermal stability is likely from a more adequate removal of unreacted monomer from the sample, preventing any trapped in the polymer matrix from off-gassing and decomposing during the measurement.

DSC analysis shows glass transition temperatures between 6.9 ˚C and 28.5 ˚C for the different samples produced in the Thrasher lab, seen in Table 3.1. Based upon the Flory-Fox equation, higher glass transition temperatures are expected for higher molecular weight samples

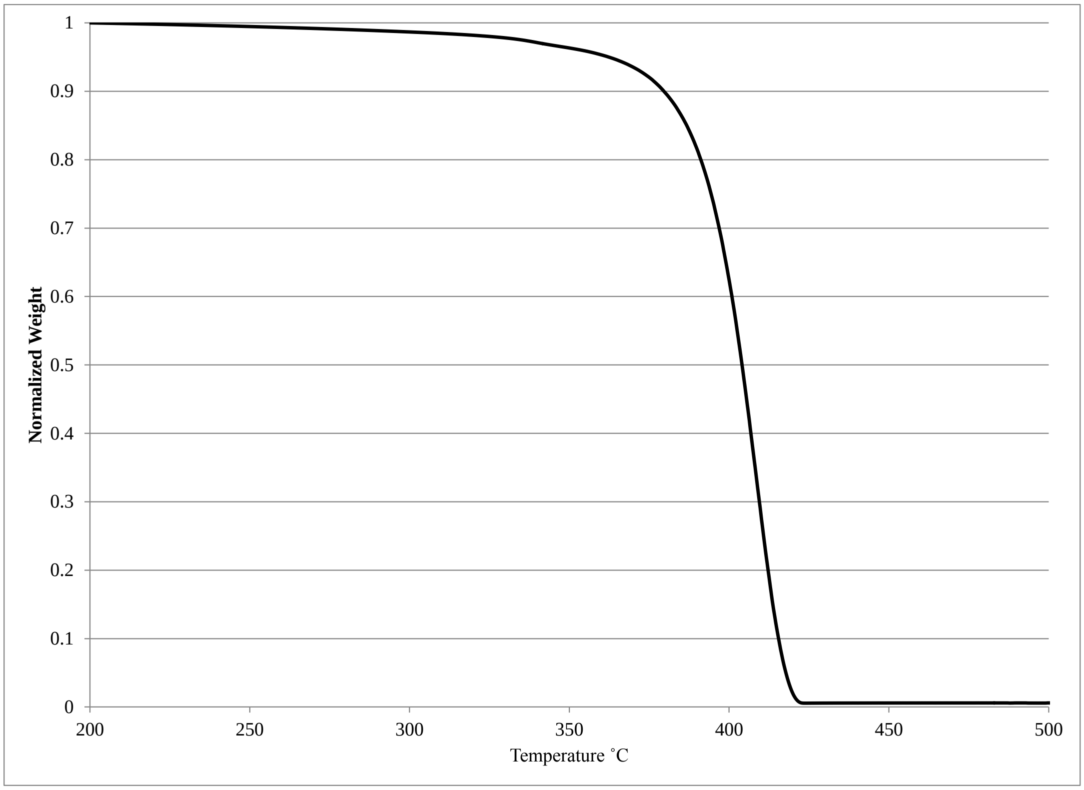

Figure 3.9. Plot of UAXH3 TGA data.

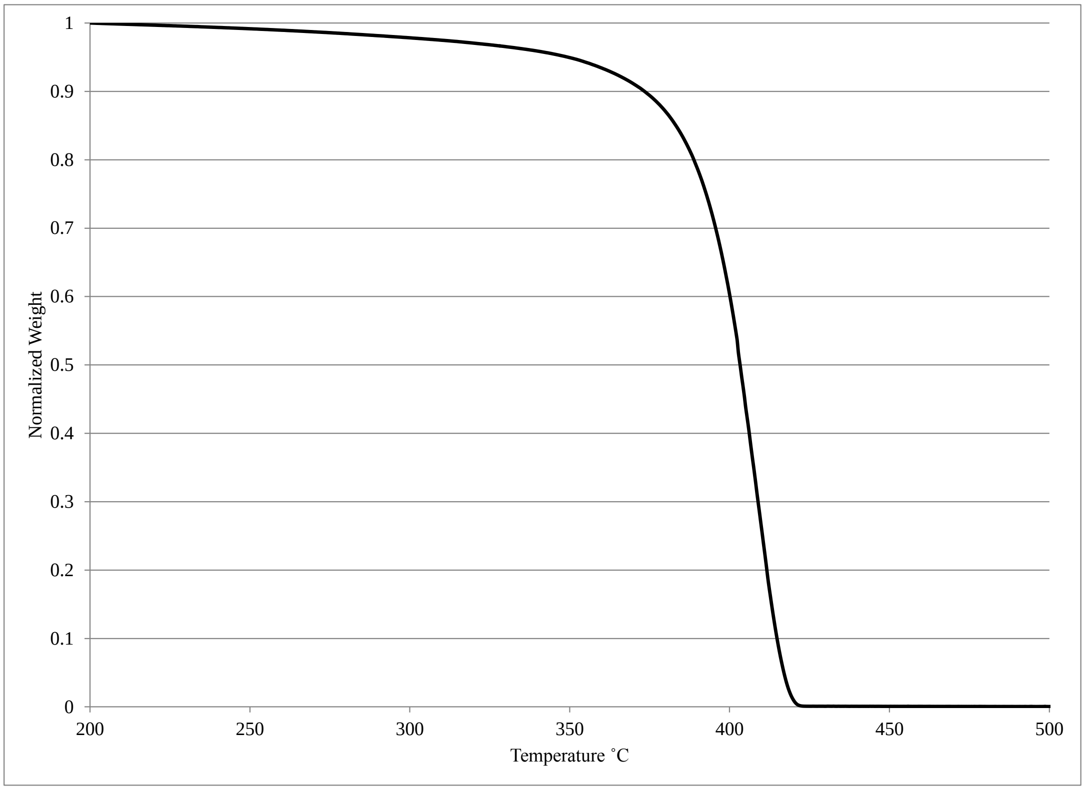

Figure 3.10. Plot of UAXDH1 TGA data.

due to the fact that higher molecular weight chains have a lower density of end groups.[11] Since the glass transition temperature is based upon the temperature where the free volume of the polymer chains reaches a minimum, preventing different chains from sliding past one another, and atoms at the end of polymer chains have a higher free volume than atoms in the backbone of the chain, higher glass transition temperatures are seen for higher molecular weight samples.[11]

Glass transition temperatures for these samples do indeed fluctuate proportionally to the expected relative molecular weights based upon the polymerization conditions. As the radical flux in the polymerization increases, i.e., increasing the rate of termination and lowering molecular weights, a lower glass transition temperature is seen. By decreasing the molar concentration of 3P in the polymerization from 10.0 to 5.3 to 2.8 mM, the glass transition temperatures increase from 17 to 20 to 25 ˚C, respectively. With a 50 ˚C polymerization temperature, where the rate of β-scission termination and radical flux both increase, the glass transition temperature is very low, 6.9 ˚C, suggesting low molecular weight. Finally, with a 5 ˚C polymerization temperature a 28.5 ˚C T_g is observed (shown in Figure 3.11), suggesting a higher molecular weight. Thus, glass transition temperatures within these samples do shift higher or lower by varying the expected molecular weight based upon the polymerization conditions, allowing the use of T_g values to predict the relative molecular weights of the samples.

The higher glass transition temperatures seen here suggest higher molecular weights than the literature material, which has a T_g of 6.9 ˚C.[5a] This is likely due to the lower radical flux in the polymerizations performed in the Thrasher group due to using more thermally stable initiators. Whereas Hsu uses the less thermally stable HFPOdp at 20 ˚C (1.9 hour half-life at 25 ˚C) and Zhang uses HFPOdp at 35 ˚C, the materials prepared here use HFPOdp as the initiator only at 5 ˚C. For room temperature (20 ˚C) polymerizations the more thermally stable

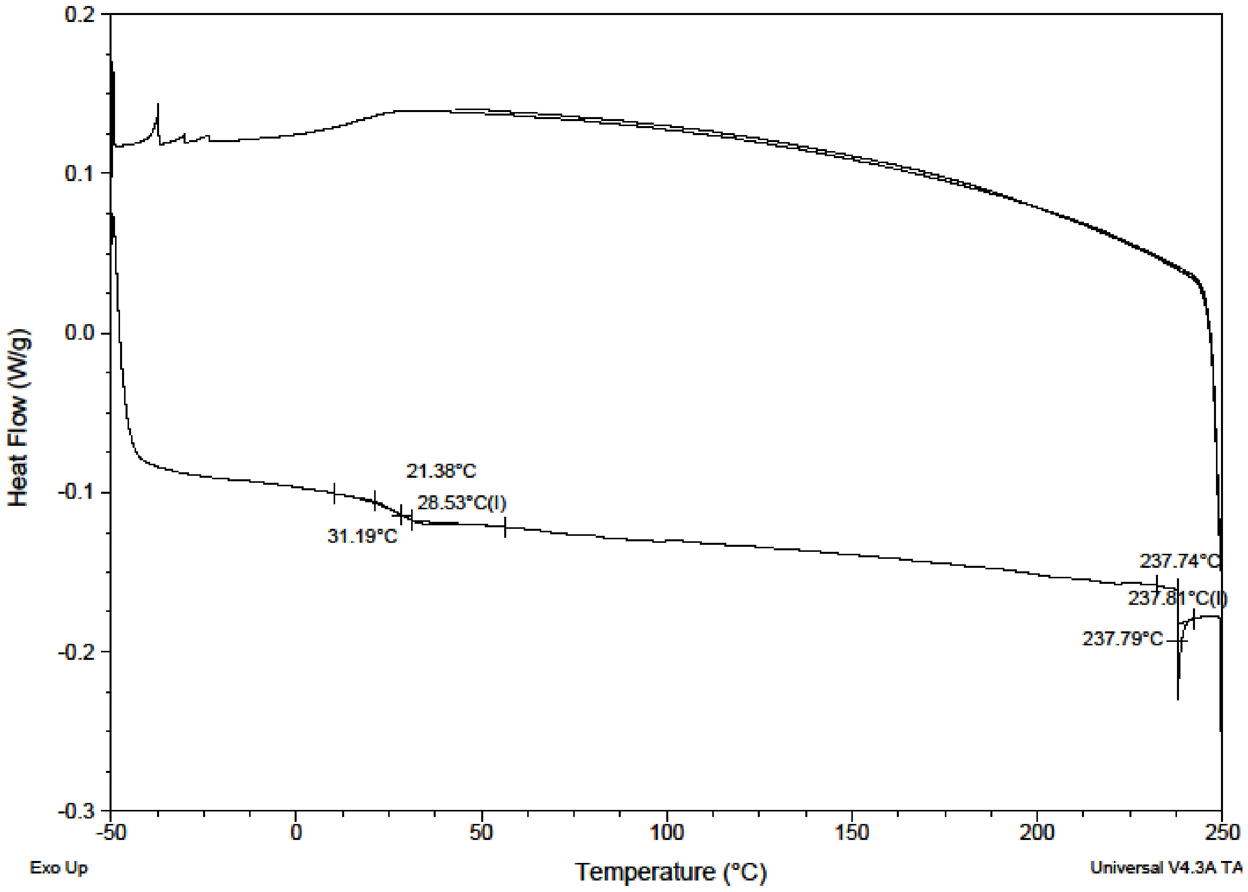

Figure 3.11. Plot of UAXH12 DSC measurement.

3P (16 hour half-life at 25 ˚C) is used. This lowers the radical flux in the polymerization, resulting in higher molecular weights by lowering the termination rate by radical combination.

Alternatively, the higher T_g's and T_d's for the samples produced by the Thrasher group could be due to a better workup procedure that removes all monomer from the polymer. Remaining monomer can act as a plasticizer, reducing the T_g, and also slowly boil away in the TGA as it escapes the polymer matrix at higher temperatures. The less intense slope of the decomposition curve from the literature suggests that the slow decomposition may be monomer slowly boiling away instead of the polymer actually decomposing.[5b] This is further substantiated by the fact that the literature homopolymer and the homopolymer produced in the Thrasher group reach the point where 90% of the sample has been decomposed at 420 ˚C and 415 ˚C, respectively. Once these polymers begin to decompose, they typically become much less stable and decompose quickly. It is unlikely that the 5% decomposition point of the literature poly(PSEPVE) is nearly 90 ˚C below the 5% decomposition point of the material prepared by the Thrasher group, and yet both materials have nearly identical 90% decomposition points.

It has been found that when the materials are not heated to at least 140 ˚C, and preferentially 150 ˚C, under high vacuum for at least 12 hours that a significant amount of monomer can be seen in the ^{19}F NMR spectrum of the unhydrolyzed resin dissolved in R113. As the monomer decomposes by rearranging into the corresponding acid fluoride when heated to 135 ˚C or higher, a workup temperature of 150 ˚C under vacuum produces the more easily removed acid fluoride. Without these conditions, high-boiling PSEPVE monomer remains in the sample, and this will change the properties of the material as well as have a significant effect on trying to crosslink the polymer to regain water insolubility as seen in Chapter 4. No analysis has been reported in the literature to date that allows for determination if all of the monomer has been removed.

3.3.3 MALDI-TOF MS Analysis of Homopolymers

Analysis of the sulfonate and sulfonamide homopolymers is further performed by matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectrometry (MS). The hydrolyzed sulfonate resins typically give a higher signal to noise ratio when examined by this technique than do the sulfonamides, so these samples were analyzed more often. Hydrolysis is performed with ammonium hydroxide, which allows removal of the excess base by distillation unlike metal containing bases such as potassium hydroxide. After hydrolysis the homopolymers become highly water soluble making water washes to remove excess base impossible. Thus, any remaining ammonium fluoride in the sample that could not be washed out likely causes lower resolution in the MALDI-TOF mass spectrum.[12] Several matrices were attempted for the samples including 2,5-dihydroxybenzoic acid (DHB), 2,5-dihydroxybenzoic acid butylamine (DHBB), and α-cyano-4-hydroxycinnamic acid (CHCA), with the best results being seen with DHB, which has been used for all the spectra presented here.

As shown using a the representative MALDI-TOF mass spectra for hydrolyzed UAXH3, shown in Figure 3.12, molecular weight distributions of the samples can be seen where the larger peak spacing corresponding to the molecular weight of the monomer. In the author’s opinion, the molecular weight distributions shown in the MALDI-TOF mass spectra likely do not accurately reflect the actual molecular weight distributions of the samples based upon literature SEC values and other properties such as T_g, T_d, and NMR spectra. Polymers with a high polydispersity index (PDI) have been shown to not accurately reflect the molecular weight distribution in MALDI.[13] With literature reported PDIs of over 2, it is likely MALDI-TOF mass

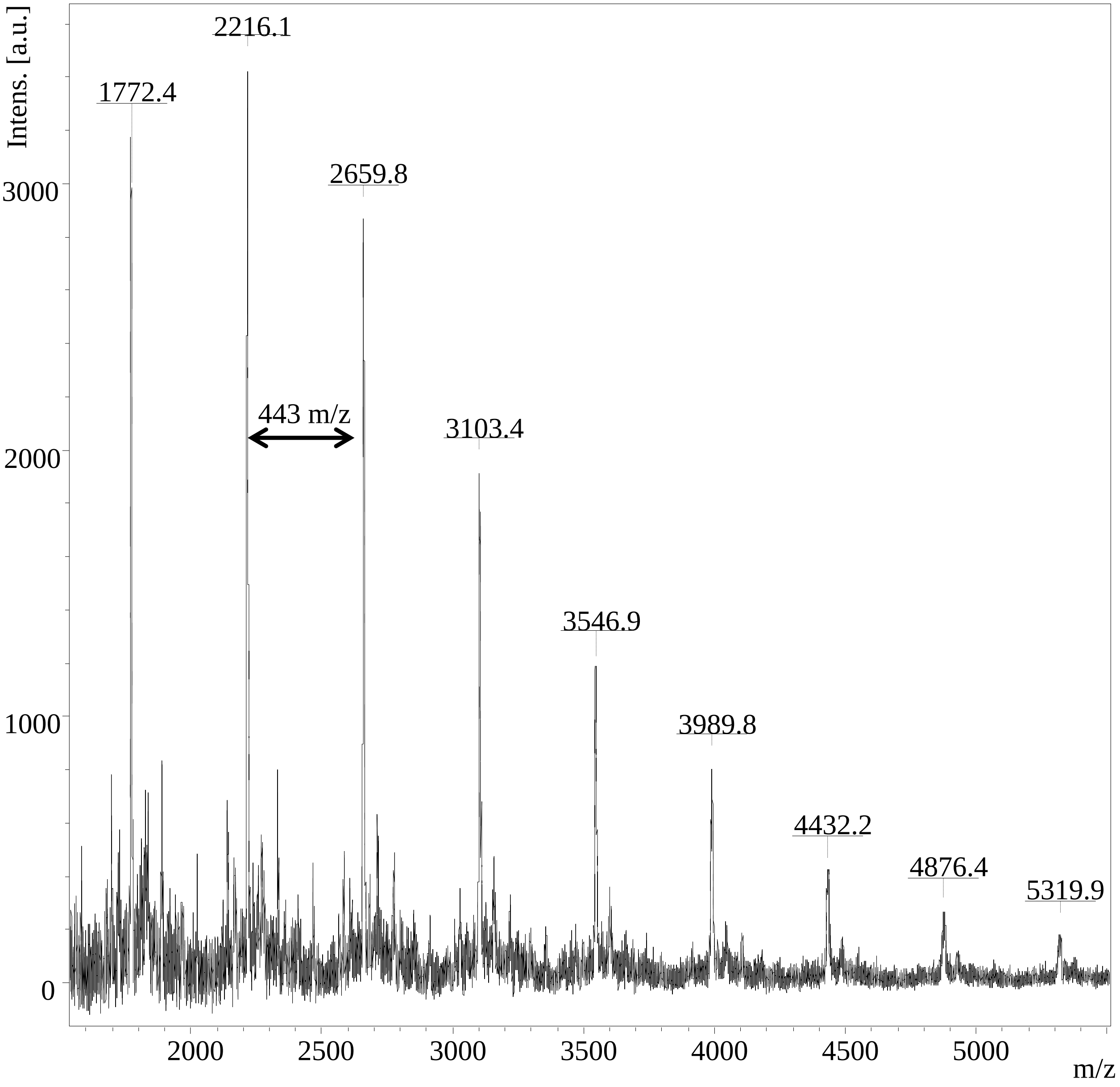

Figure 3.12. UAXH6H MALDI-TOF mass spectrum.

spectroscopy gives an inaccurate molecular weight distribution for these types of polymers. The smaller clusters of peaks represent polymer chains with the same number of monomer units but different end groups, allowing characterization and quantification of the end groups on the polymer chains and giving insight into the actual mechanism of the polymerization.

For UV initiated polymerizations only a single set of end groups exists with all chains separated by 443 m/z, as seen in Figure 3.12. It appears from the MALDI-TOF mass spectrum that the UV light initiates a $\pi \rightarrow \pi^*$ transition the vinyl functional group, which undergoes a β-scission reaction to generate an alkyl radical, $FSO_2CF_2CF_2OCF(CF_3)CF_2\cdot$, termed β_{PS}. This alkyl radical initiates the polymerization, which based upon the low yield, long reaction time, and MALDI-TOF mass spectrum is nearly exclusively terminated by another β-scission to yield acid fluoride terminated polymer chains and another β_{PS} alkyl radical that can initiate new chains.

The workup procedure converts any acid fluoride to a carboxylic acid during the hydrolysis step. Carboxylic acid end groups present their own problems inside an actual fuel cell as peroxides which can be formed from the reaction of oxygen with protons and electrons at the cathode catalytically decompose the polymer from these acid end groups.[14] Chain-transfer of the proton from the carboxylic acid generates a carboxylic acid radical, a transient species that eliminates CO_2 to give the alkyl radical. This alkyl radical reacts with a hydroxyl radical to form an acid fluoride that is then hydrolyzed to give the starting carboxylic acid again.[15] The polymers could either be treated with ethanol to form the ethyl ester or elemental fluorine to yield perfluorinated end groups that are more stable in the fuel cell environment; however, these treatments were not performed here as the materials were not actually tested in a fuel cell and insufficient time and manpower was available. While both the β-scission reactions and the formation of acid end groups that can cause catalytic decomposition of the polymer in fuel cell applications[15] are well known to occur during polymerization of PSEPVE, no mention exists in the literature of the resulting β_{PS} subsequently initiating or terminating chains or it being the limiting factor in increasing molecular weights of the homopolymers.

As seen in Figures 3.13 - 3.16, for 3P initiated polymerizations an increase in the diversity of end groups is seen over the UV initiated polymerization seen in Figure 3.12, corresponding to two different initiation mechanisms, 3P and β_{PS} radicals, and up to four termination mechanisms, 3P, β_{PS}, β-scission, and chain transfer from hydrocarbons. Chain transfers can be eliminated by using a perfluorinated solvent for the initiator solution. This difference can be seen when comparing Figure 3.14, the MALDI-TOF spectrum of sample UAXH2 where HFC-4310 is used as the initiator solvent, and Figure 3.16, the MALDI-TOF spectrum on a sample from a polymerization performed with perfluorohexane as the initiator solvent. The absence of the peak at 2777 m/z when using perfluorohexane shows the removal of the chain-transfer termination route, thereby increasing molecular weight.

Examination of the MALDI spectra shows the β-scission termination is the main cause for the low molecular weights of the homopolymers. For example, in Figure 3.16 the intensity of the β-scission terminated peaks (2432 and 2660 m/z) are roughly three to four times higher than peaks terminated with β_{PS} or 3P radicals (2458 and 2684 m/z). In most polymerizations, the molecular weight can be tuned by changing the radical flux within the reaction. By lowering the radical flux the rate of termination is decreased and polymers have higher molecular weights. Here the rate of β-scissions is independent of the radical flux and depends only upon the temperature. This fact, combined with the low reactivity of the PSEPVE monomer towards homopolymerization means that significant increases in molecular weight are not possible by simply changing the concentration of radicals in the reaction mixture.

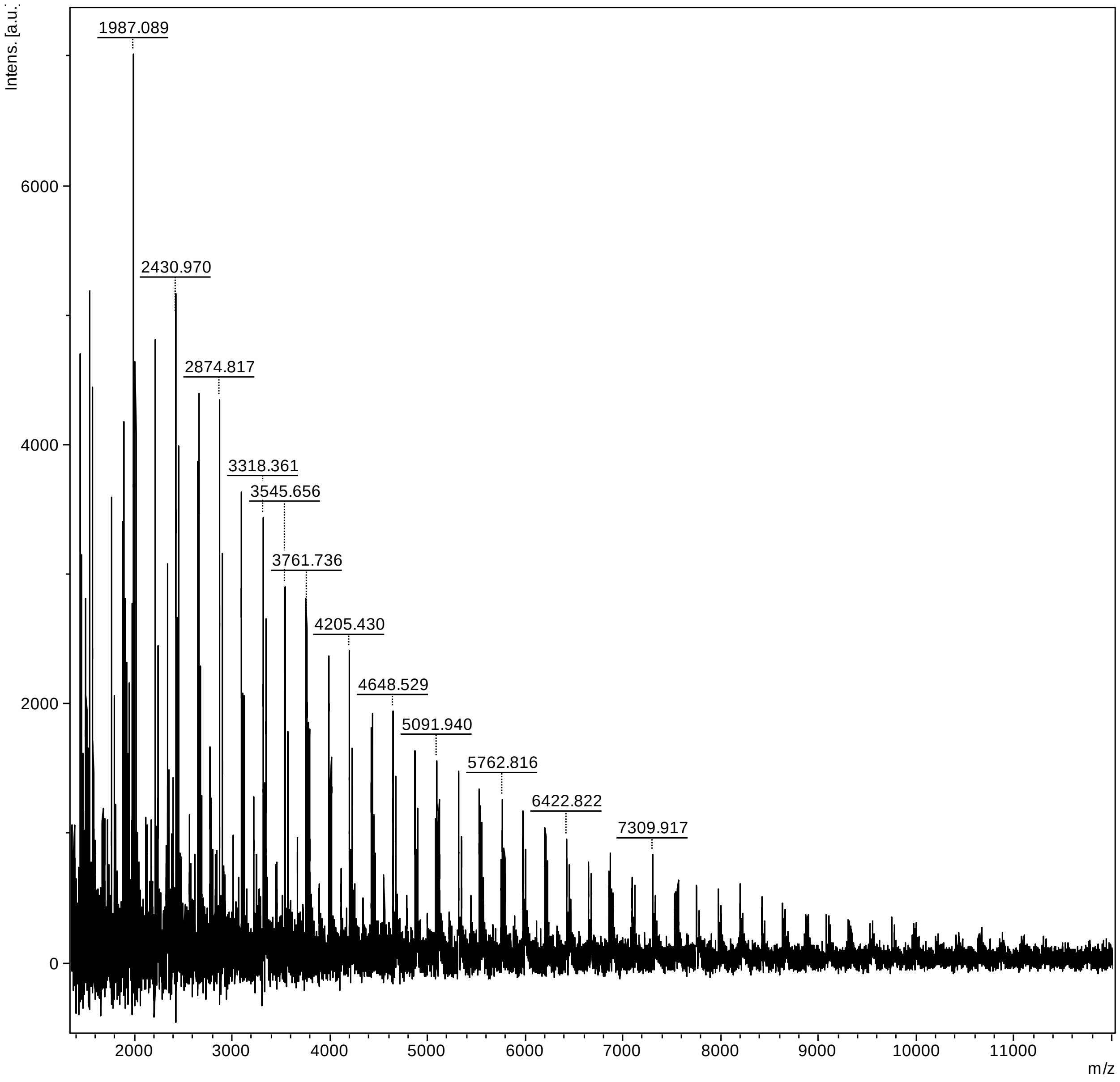

Figure 3.13. UAXH2H MALDI-TOF mass spectrum

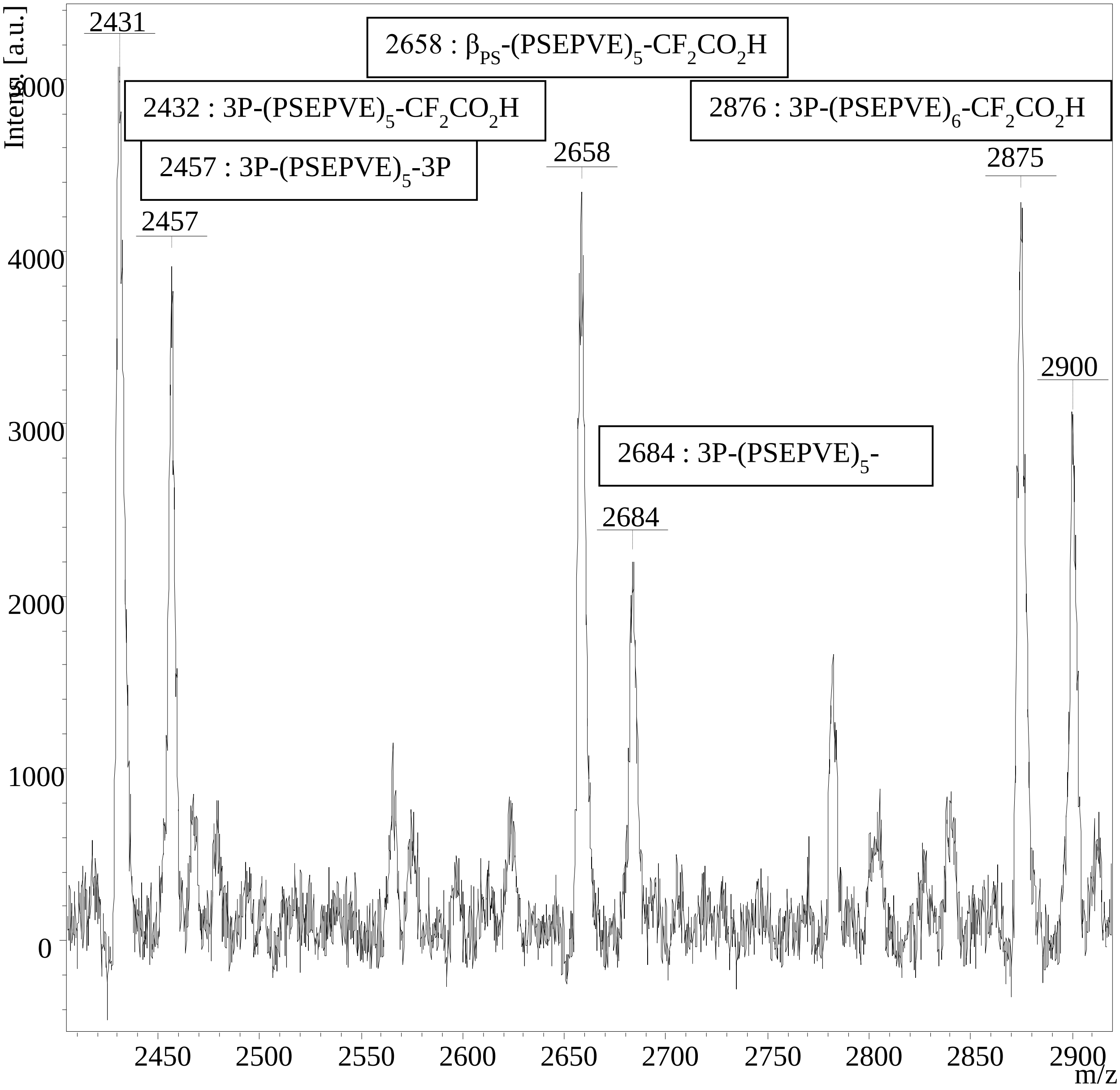

Figure 3.14. Expansion of UAXH2H MALDI-TOF mass spectrum.

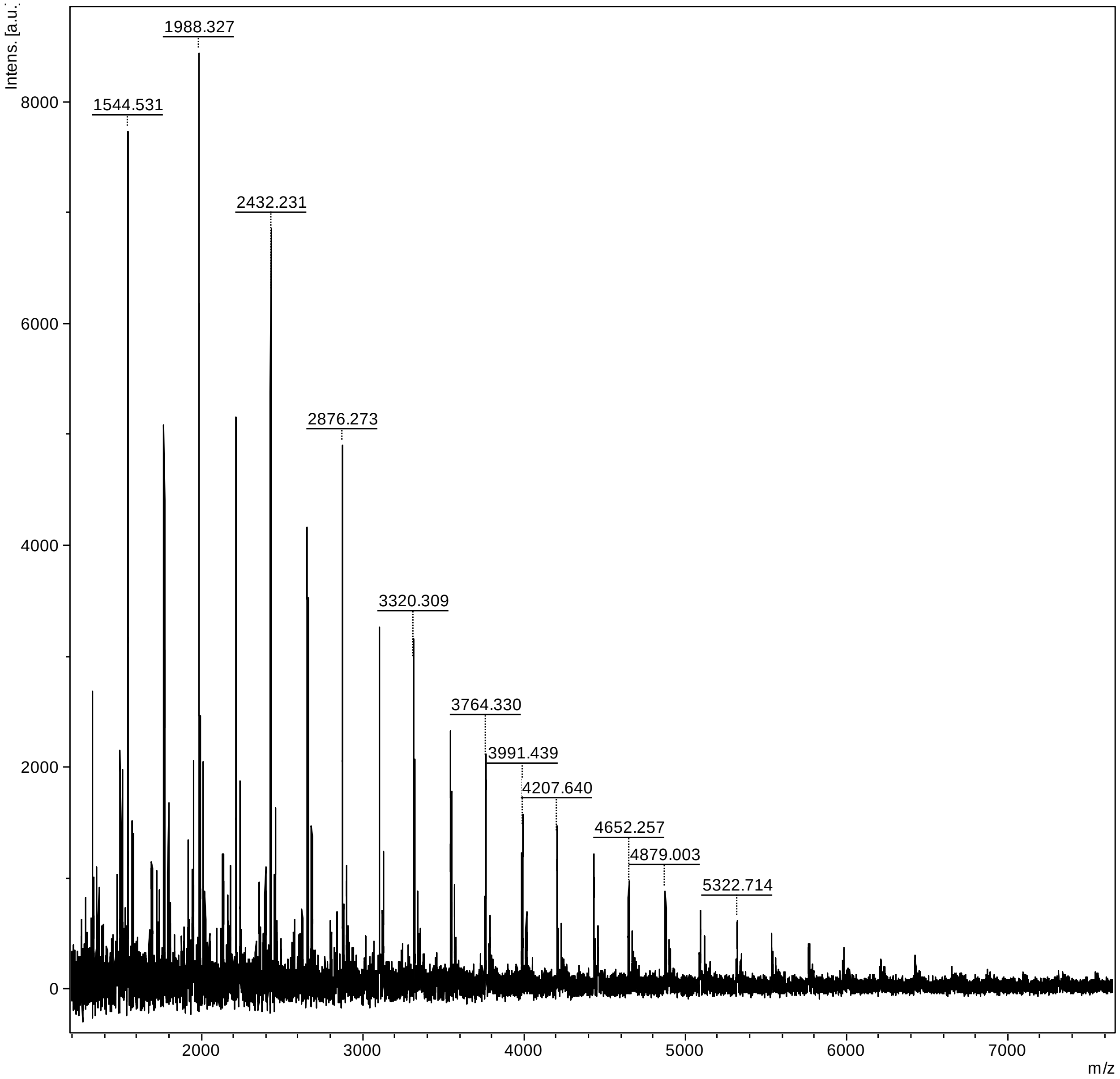

Figure 3.15. UAXH3H MALDI-TOF mass spectrum.

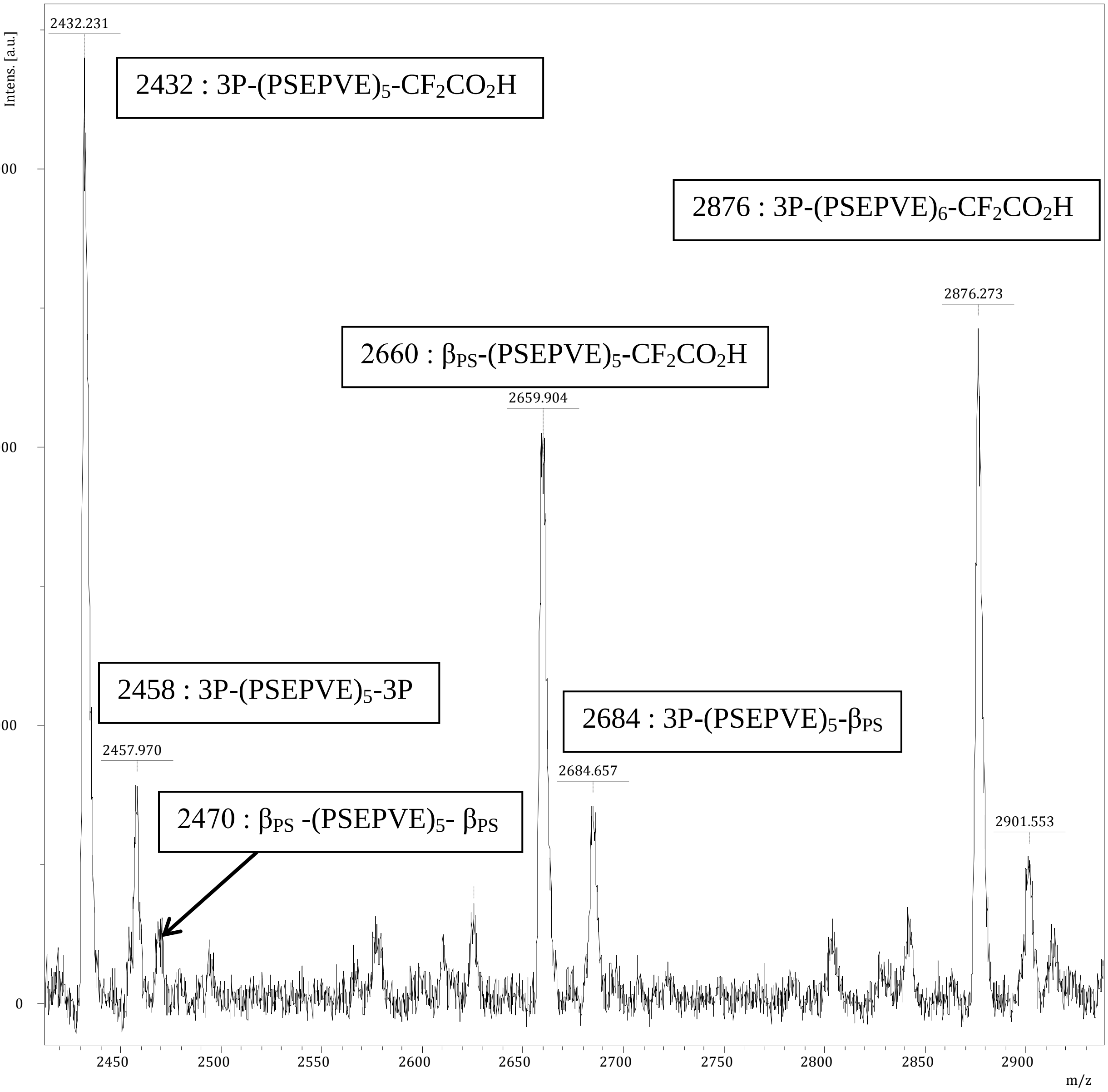

Figure 3.16. Expansion of UAXH3H MALDI-TOF mass spectrum.

By analyzing the intensity of chains with carboxylic acids or β_{PS} end groups compared to 3P end groups, one can get an estimate of just how much the β-scission termination limits molecular weight. For example, in Figure 3.16, it can be seen that the most intense peaks occur from carboxylic acid terminated chains. The intensity of 3P initiated and carboxylic acid terminated chains, seen at 2432 m/z in Figure 3.16, is nearly five times higher than the intensity of chains initiated and terminated by 3P, seen at 2458 m/z in Figure 3.16. This ratio suggests the rate of β-scission terminations is so high that the molecular weights of the polymers are lowered by a factor of six from the expected molecular weights based on the radical flux.

As both the rate of polymerization and β-scission are temperature dependent, polymerizations at 50 ˚C and 5 ˚C were performed to see if the rate of polymerization could be increased relative to the rate of β-scission termination by altering the reaction temperature. The sample from a polymerization performed at 50 ˚C shows both a low glass transition temperature at 6.9 ˚C, a lower molecular weight distribution in the full MALDI spectrum (see Figure 3.17) as well as a high ratio of β_{PS} initiated chains compared to 3P initiated chains in the expanded MALDI spectrum (see Figures 3.18), suggesting a high rate of β-scission termination and low molecular weight. Samples from polymerizations carried out at 5 ˚C show both a higher glass transition temperature of 28.5 ˚C and a lower ratio of β_{PS} initiated chains compared to 3P initiated chains, as shown in Figures 3.19 and 3.20, suggesting a lower rate of β-scission termination and higher molecular weights. However, based upon the low rate of polymerization, especially at 5 ˚C, the difference between the molecular weights of the samples prepared at the two different temperatures do not appear to be large based upon the author's opinion. Unfortunately this could not be confirmed by GPC measurements to show molecular weight distributions and their melt flow characteristics are far too high to compare to the copolymers.

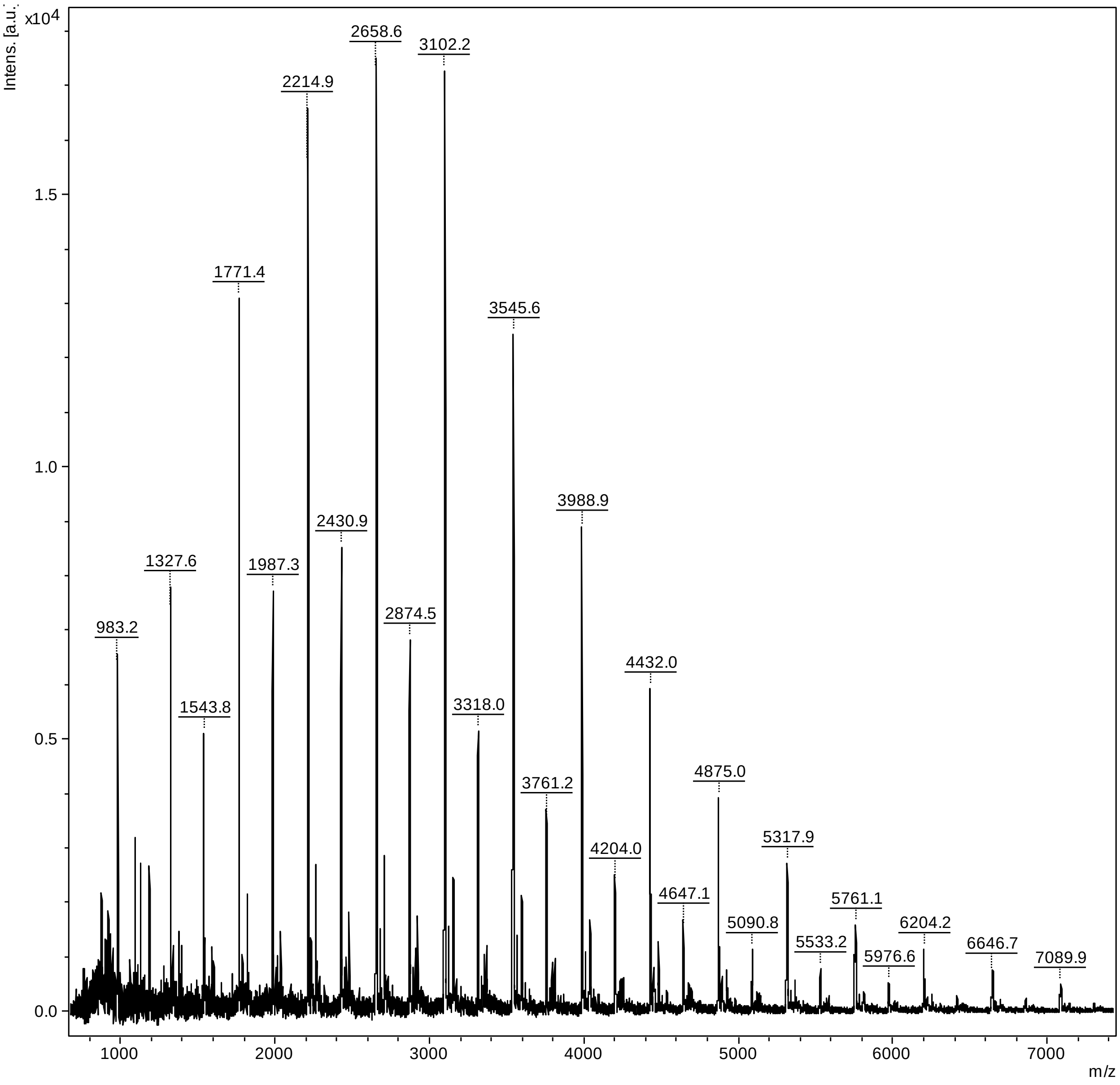

Figure 3.17. UAXH4H MALDI-TOF mass spectrum.

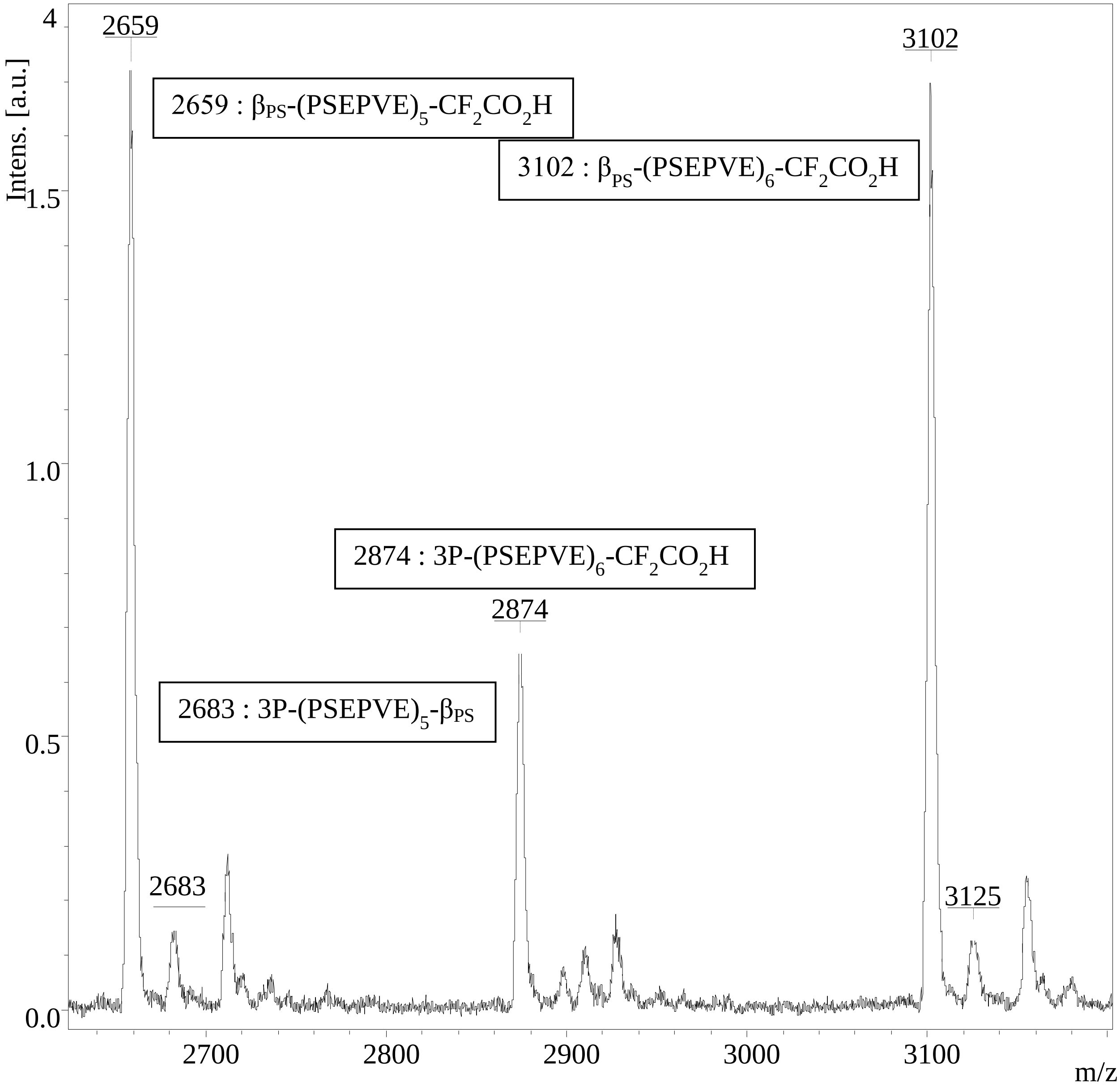

Figure 3.18. Expansion of UAXH4H MALDI-TOF mass spectrum.

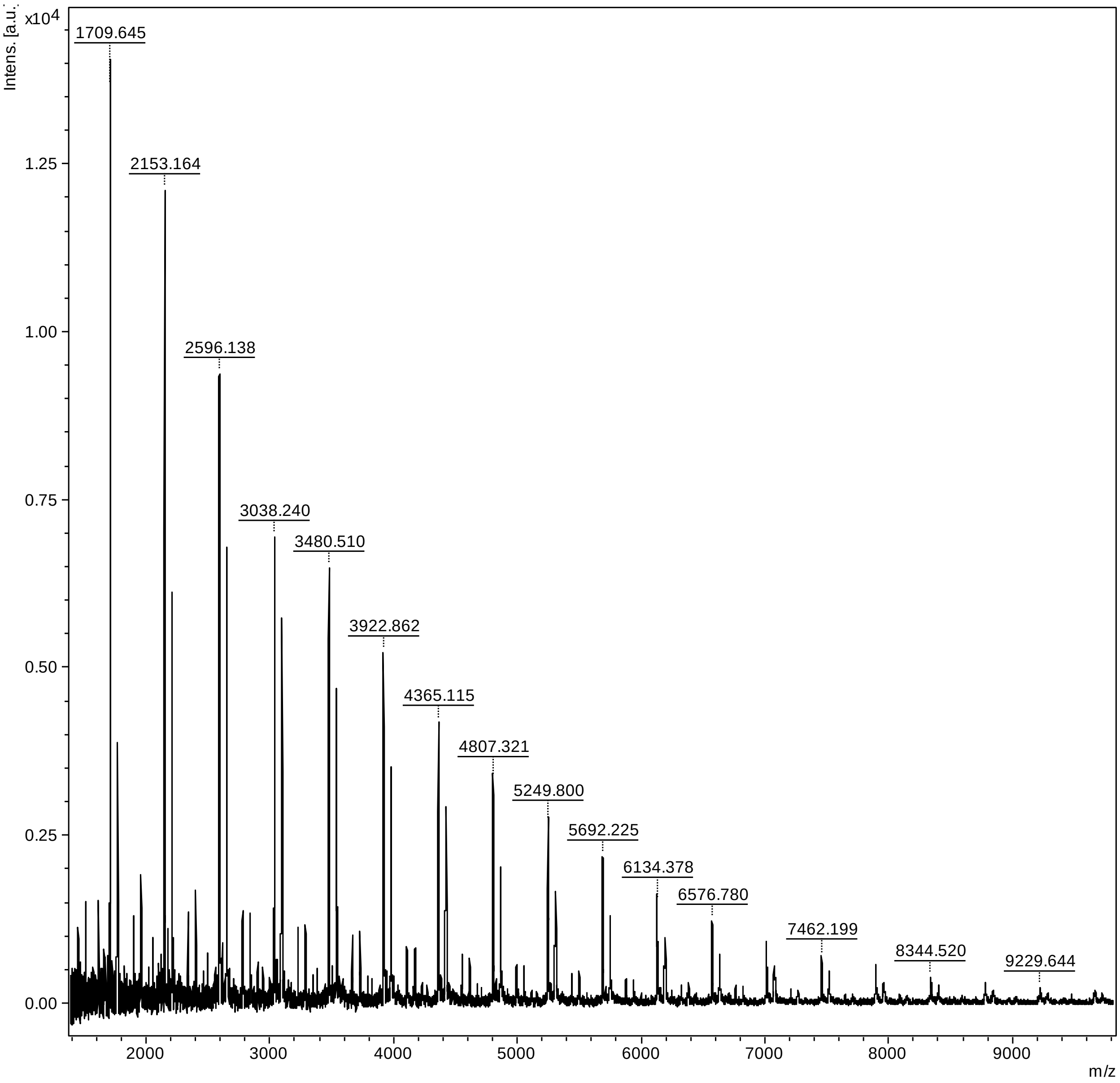

Figure 3.19. UAXH12H MALDI-TOF mass spectrum.

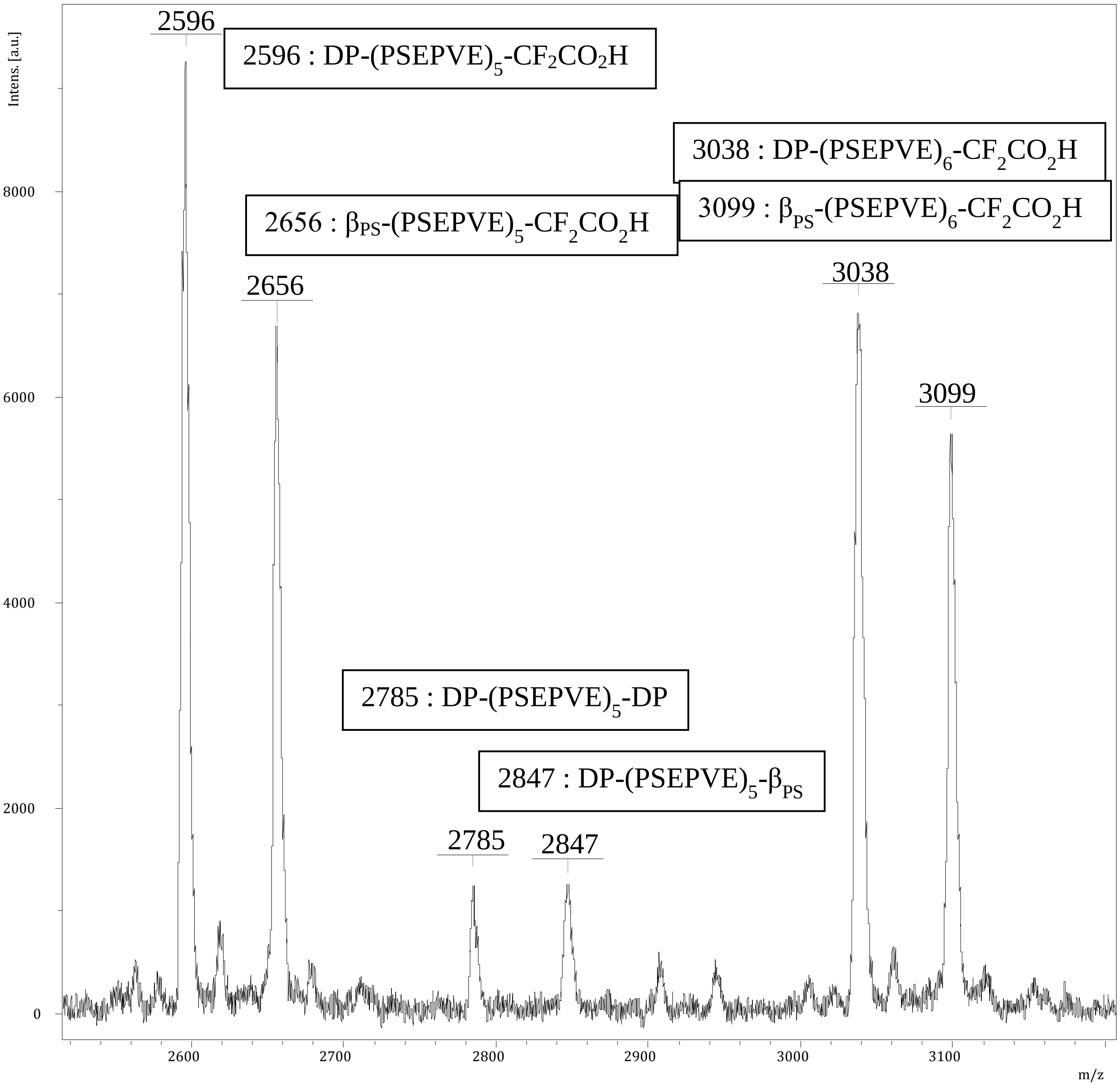

Figure 3.20. Expansion of UAXH12H MALDI-TOF mass spectrum.

Intrinsic viscosity measurements would likely have too large of an error bar to tell small differences in molecular weights between the samples and were not attempted.

It has been hypothesized that with a shorter side chain, poly(Dow) may produce higher molecular weight samples. MALDI spectrum of sample UAXDH1, the homopolymer of the Dow vinyl ether monomer, appears to confirm this hypothesis. Figure 3.21 shows a higher molecular weight distribution by MALDI-TOF mass spectroscopy than the MALDI spectrum for sample UAXH2, prepared under the same conditions except with PSEPVE instead of Dow vinyl ether monomer. This difference in molecular weight distribution is more pronounced when taking into account the lower molecular weight of the Dow vinyl ether (280 g/mol) than PSEPVE (446 g/mol), showing a higher number of repeat units for the poly(Dow) material. The expansion of poly(Dow) (shown in Figure 3.22) shows the high rate of β-scission termination still likely produces a material more towards an oligomer than a polymer.

The measurement of molecular weights by GPC along with correlation of molecular weights to properties, especially conductivity, should be a useful direction for future work in this area. Little to no work has been done comparing molecular weights of these homopolymers or the aforementioned copolymers (see Chapter 2) to fuel cell properties, which would likely prove valuable basic knowledge in this area. With GPC it may also prove possible to determine the maximum molecular weights that can be obtained for poly(PSEPVE) and poly(Dow) and give the ability to correlate the MALDI-TOF spectrum to more reliable measurements.

MALDI-TOF mass spectroscopy and GPC could also further complement each other by allowing a correlation of the monodisperse polystyrene GPC standards to the molecular weights of the fluoropolymer seen in both the GPC and MALDI-TOF mass spectrometry. GPC separates polymers based upon how easily they enter different sized pores in the column, with high

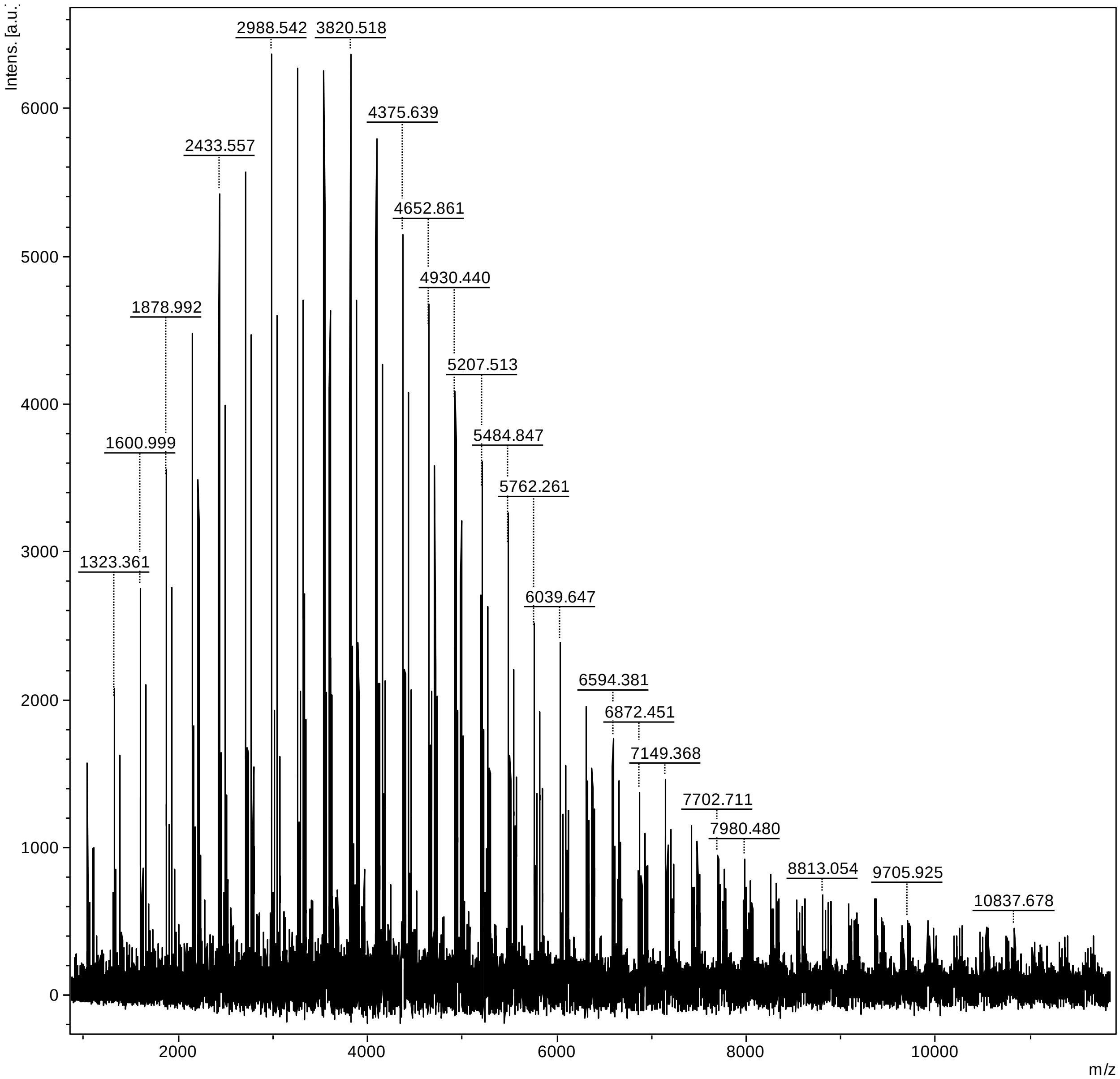

Figure 3.21. UAXDH1H MALDI-TOF mass spectrum.

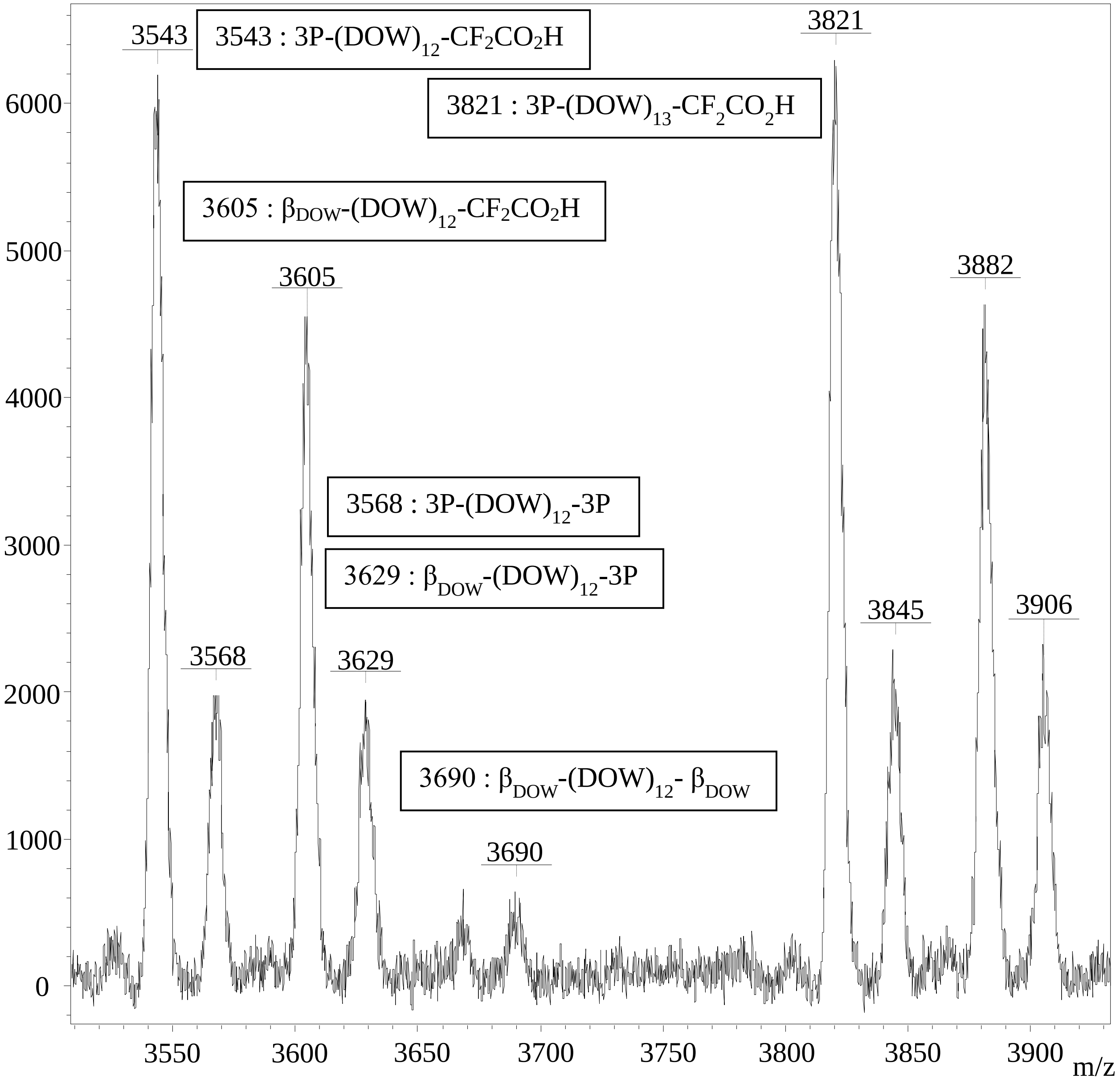

Figure 3.22. Expansion of UAXDH1H MALDI-TOF mass spectrum.

molecular weight samples eluting first and low molecular weight samples eluting last. Fluoropolymers show very different structures than hydrocarbon polymers, such as PTFE having a helical structure with only around 20˚ rotation between each CF_2 group compared to the zig-zag structure of polyethylene. Additionally, while hydrogen and fluorine have similar van der Waals radii, fluorine has an atomic mass 19 times greater, suggesting the GPC would likely under-estimate the molecular weight when using a polystyrene reference standard. GPC could be used to mass fractionate the different samples of polymers to make each cut more monodisperse. MALDI-TOF mass spectroscopy of these more monodisperse samples should then allow more accurate determinations of the molecular weights of the samples without mass discrimination. Using these accurate molecular weights, one should be able to calibrate the polystyrene samples more accurately to the molecular weights of the fluoropolymers. This would allow more accurate mass molecular weight characterization of fluoropolymers by GPC than is currently reported in the literature[5b] where monodisperse polystyrene is used as a reference with no adjustment for the differences in structure of polystyrene and fluoropolymers.

3.3.4 Homopolymer Conclusions

PSEPVE has been homopolymerized using a bulk polymerization with varying temperatures and initiator concentrations as well as with UV initiation. A proper workup procedure has been found to remove all remaining monomer from the polymer produced, thereby allowing accurate T_g and T_d values to be measured as opposed to literature reports that have incorrect values due to monomer contamination.[5] Additionally, the MALDI-TOF mass spectra of the samples have been measured, providing insight into the high amount of β-scission terminations that results in low molecular weight oligomers being produced as opposed to true polymers. Analysis of these materials offers insight into the preparation of low equivalent weight polymers of this type and what conditions are needed to obtain better low EW polymers. If a method to crosslink these chains together can be found, similar to what will be described in Chapter 4, then it may be possible to produce extremely low EW, water insoluble materials using these types of materials.

3.4. References

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CHAPTER 4

PREPARATION OF POLYMERS CONTAINING CURE-SITE MONOMER

4.1 Introduction

Homopolymerization of both PSEPVE and Dow monomers yields materials that are highly soluble in water after hydrolysis due to both the low crystallinity and low molecular weight.[1] In order to produce low equivalent weight (below 700 g/mol) ionomers that are insoluble in boiling water for 24 hours, new methods must be found to either increase molecular weights or crystallinity in the polymer for low EW samples. Increasing crystallinity with such low TFE concentrations is difficult; however, patents from W. L. Gore and Associates show that using a mini-emulsion polymerization produces lower EW materials which still have some crystallinity present.[2] The other route to obtain water insolubility is to produce a material with an extremely high molecular weight, such that entropy prevents dissolution. One method to produce such high molecular weight samples is to crosslink the polymers to produce a networked structure with a molecular weight that is effectively infinite, limiting the solubility of the polymer due to entropic effects.

Many different curable monomers exist in the literature that allow crosslinking of perfluorinated polymers.[3] One commonly used monomer in the preparation of fluoroelastomers is perfluoro 8-cyano-5-methyl-3,6-dioxa-1-octene (8CNVE), which is used commercially in DuPont's Kalrez® product line.[4] Kalrez® is typically a terpolymer of TFE, a perfluoro(alkyl vinyl) ether or perfluoro(alkoxy vinyl) ether, and a curable monomer such as 8CNVE. Curing is performed by converting the nitrile functional group to a triazine using a suitable Lewis acid catalyst, typically tetraphenyl tin or silver oxide at elevated temperatures under pressure.[3c,5]

More recent art shows that a nitrogen containing compound can be added to the curing step to increase the rate of curing significantly.[6]

Curing to form the aromatic triazine has several benefits such as high chemical and thermal stabilities as well as the ability to crosslink three chains instead of just two chains seen with most other crosslinking agents.[4] Crosslinking three chains through a triazine produces a higher degree of crosslinking with the same amount of cure-site monomer in the polymer. This allows lower EW materials to be prepared since less of the cure-site monomer is needed for the same crosslink density. However, a downside is any remaining nitrile functional groups after curing will be hydrolyzed to amides during hydrolysis. Amides likely possess low chemical stability during fuel cell operation similar to carboxylic acids, and thus the end result will be low membrane lifetimes.

Crosslinking to a sufficiently high degree that all polymer chains are covalently bonded produces what is termed a networked polymer. With these materials the entire sample is a single molecule, making molecular weights effectively infinite. With such high molecular weights the entropy of solution begins to trend towards zero such that there is no net entropic gain from the molecules dissolving, making these sorts of materials insoluble.[7] However, as the enthalpy of solution has not changed, highly hydrophilic polymers that are crosslinked tend to retain large degrees of water swelling, as evidenced by hydrogels.

Patent art already exists that claims all perfluorinated polymers used as polymer electrolyte membranes that are crosslinked through triazines.[8] Yet no example, characterization or analysis of the material is given in the patent and the only hint at the equivalent weights explored exists as legal jargon:

> “The acid-functional pendant groups typically are present in an amount sufficient to result in an equivalent weight (EW) of less than 1200, more typically less than 1100, and more typically less than 1000, and more typically less than 900.”

As the patent inventors are 3M employees the material being investigated is likely the 3M monomer, perfluoro-4-(fluorosulfonyl) butyl vinyl ether, which does not show water solubility until an EW of 800 g/mol. As no mention is made of EWs below this value, it may be inferred the only materials studied are those that are water insoluble before crosslinking. Additionally, no characterization of the materials is given to show the validity of using these types of materials in fuel cells or their properties. Thus, the Thrasher group began investigating the preparation of polymers with low EWs, more specifically polymers that contain the 8CNVE cure-site monomer that upon conversion to the triazine gives water insoluble membranes for fuel cell applications, following the reaction schematic shown in Figure 4.1.

The nomenclature of these materials is similar to that as described in Chapter 2. All polymer samples begin with UAX for University of Alabama eXperimental. Copolymers prepared with PSEPVE are then labeled UAXR while materials prepared with Dow are labeled UAXD. Polymers without any TFE incorporation are labeled UAXH and UAXDH for the PSEPVE and Dow homopolymers, respectively. Addition of a C indicates cure-site monomer 8CNVE has been added such that UAXDHC represents a polymer containing Dow monomer without any TFE, but with 8CNVE cure-site monomer added, and UAXDC corresponds to a terpolymer prepared with the Dow monomer. These letters are followed by a number that indicates the individual polymer sample. Adding another C after this number indicates the sample is cured, and the subsequent number indicates the individual curing reaction and sample. Adding eP indicates the polymer is impregnated within an ePTFE mat to form a composite.

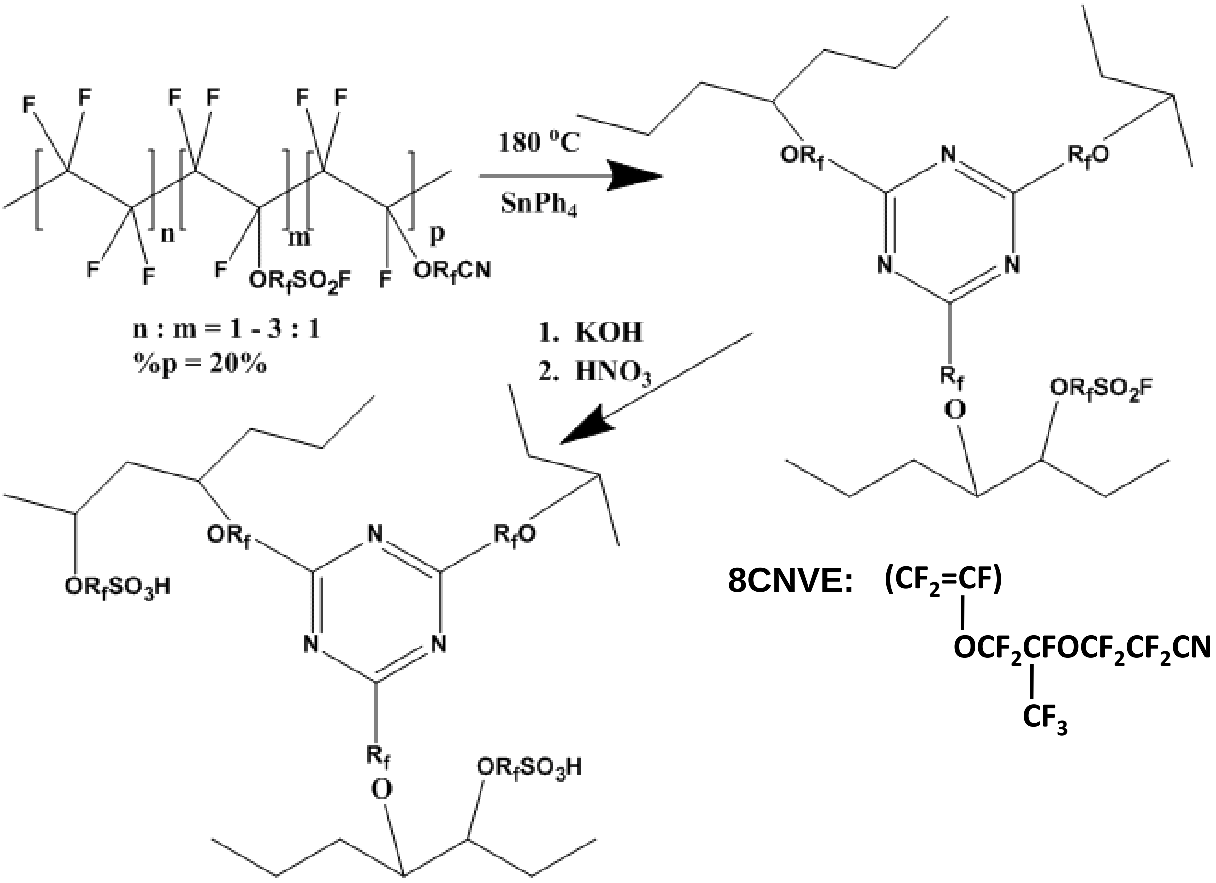

Figure 4.1. Structure of 8CNVE and reaction schematic.

4.2 Experimental

4.2.1 Copolymerization of PSEPVE and 8CNVE

Similarly to Example 3.1.6, 226.1 g of PSEPVE and 48.13 g of 8CNVE that have been previously degassed by the freeze/pump/thaw method are added to the FEP reactor vessel seen in Figure 3.1. With a nitrogen pad on the system, 1.5 mL of a 0.106 M solution of 3P in perfluorohexane is added every 24 hours for 6 days, giving a molar ratio of monomer to initiator per addition of 4000 to 1. After 8 days the volatile contents are removed from the reactor while holding the mixture at 150 ˚C and 100 mtorr overnight yielding 21.05 g of UAXHC1. Five samples have been prepared by this method with different concentrations of 8CNVE, as shown in Table 4.1.

$\{CF_2^aCF^b[OCF_2^cCF^d(CF_3^e)OCF_2^fCF_2^zCN]\}_m$ ^{19}F NMR spectroscopy of UAXHC2 dissolved in R113: δ^a -105 to -118 (broad); δ^b -137.3 (1F, broad); δ^c -80.6 (4F); δ^d -144.7 (1F); δ^e -79.7 (3F); δ^f -80.6 (4F); δ^h 43.1 (1F); δ^y -112.9 (1.78F); δ^z -108.9 (0.22F).

Table 4.1. Syntheses of Poly(PSEPVE-co-8CNVE)

Sample	PSEPVE (g)	8CNVE (g)	mol% 8CNVE monomer	Product (g)	mol% 8CNVE in polymer
UAXHC1	130	22.7	17	14.12	18.3
UAXHC2	140	12.2	9.1	15.61	11.0
UAXHC3	150	6.5	4.7	16.09	5.35
UAXHC4	226	48.1	20.	21.05	19.7
UAXHC5	140	18.3	13	17.03	12.8

4.2.2 Copolymerization of Dow and 8CNVE

Copolymerization of Dow and 8CNVE is carried out similarly to Example 4.2.1 with 77.25 g of Dow vinyl ether and 18.56 g of 8CNVE (14.7 mol%). Six aliquots of a 0.106 M solution of 3P in perfluorohexane are added every 24 hours. After workup, 5.64 g of copolymer is recovered that contains 17.3 mol% 8CNVE by ^{19}F NMR spectroscopy (see Table 4.2).

Table 4.2. Synthesis of Poly(Dow-co-8CNVE)

Sample	Dow (g)	8CNVE (g)	mol% 8CNVE monomer	Product (g)	mol% 8CNVE in polymer
UAXDHC1	77.25	14.7	14.7	5.64	17.3

4.2.3 Terpolymerization of Dow, 8CNVE, and TFE

Dow and 8CNVE monomers are degassed as previously stated. To a 100-mL stainless steel autoclave in a drybox is added 62.04 g of Dow vinyl ether and 18.48 g of 8CNVE. The autoclave is sealed, and the TFE polymerization system is prepared as described in Chapters 1 and 2 with the Ascarite II® CO_2 scrubber installed and the autoclave kept at 18 ˚C, room temperature. The polymerization is performed with the pressure of neat TFE in the autoclave vapor space kept around 42 psig throughout the reaction as seen in Table 4.3. Approximately every 24 hours 1.0 mL of a 0.106 M solution of 3P in perfluorohexane is added using a Teledyne ISCO HPLC pump for five days. Workup is performed similarly to Example 4.2.1 yielding 25.38 g of UAXDC1. Equivalent weight titrations, as described in Example 4.2.13, show the sample to have an EW of 640 g/mol, similar to that predicted by NMR spectroscopy for the sample dissolved in R113. Four terpolymer samples have been prepared as shown in Table 4.4 with varying ratios of the monomers.

$$\{CF_2^aCF^b[OCF_2^cCF_2^ySO_2F^h]\}_n\{CF_2^aCF^b[OCF_2^cCF^d(CF_3^e)OCF_2^fCF_2^zCN]\}_m\{CF_2^qCF_2^q\}_p$$

^{19}F NMR spectroscopy for UAXDC1 dissolved in R113: $\delta^{a,q}$ -118.1, -120.7, -121.8; δ^b -137.7; δ^c -80.01; δ^d -144.3; δ^e -78.1; δ^f -84.5; δ^h 43.1; δ^y -112.3 (1.66 F); δ^z -108.6 (0.34 F).

ATR-FTIR Analysis (cm^{-1}): 2268 (w); 1467 (s); 1323 (w); 1184 (s); 1143 (s); 1036 (w); 984 (w).

Table 4.3. UAXDC1 Polymerization Run Sheet. Notes: "Entire system open" denotes the BPR dome pressure is removed and valve TFE 2 is open, increasing the total volume of the vapor space. "Slow bleed" denotes adding 200 psig nitrogen to the BPR dome and slowly bleeding.

Day	Time	Autoclave (psig)	TFE 1 (psig)	Notes
1	15:20	17	64	Added 1.25 mL initiator
	15:23	31	32	
	15:25	42	93	
	15:30	35 → 41	74	
	16:19	27 → 42		
	16:25	40 → 42		
	16:57	33 → 42		
	17:40	36 → 42		
	17:50	40 → 44	57	Slow bleed to drop BPR overnight
2	16:11	35 → 42	36	
	16:45	39 → 42		1.0 mL initiator
	16:52	41	51	
	16:54	41	77	
	16:56	43	70	Slow bleed
3	16:52	34 → 43	35	
	17:03	41 → 42		1.0 mL initiator
	17:19	40 → 43	50	Slow bleed
4	8:12	33 → 43	34	1.0 mL initiator
	10:30	35 → 42	44	Entire system open
	13:19	36 → 42	39	
	15:25	37 → 42		
	17:30	38 → 42	59	1.0 mL initiator, entire system open
	18:09	39 → 42	62	Slow bleed
5	8:05	36 → 42	37	
	9:00	38 → 42		
	10:27	38 → 41	50	Entire system open
	10:55	40 → 43	41	
	11:40	41 → 44	50 - 45	Entire system open
	13:13	40	42	
	14:28	40	41	
	15:41	39 → 42	44	Entire system open
	16:58	40 → 43	41 - 61	Add 0.8 mL initiator
	17:26	41 → 43		Entire system open
6	8:16	35 → 43	36	Workup begun

Table 4.4. Syntheses of Poly(TFE-ter-Dow-ter-8CNVE)

Sample	Dow (g)	8CNVE (g)	TFE (psig)	Yield (g)	TFE : Dow : 8CNVE (molar)	EW (g/mol)
UAXDC1	62	19	50	25	3.0 : 1.0 : 0.20	640
UAXDC2	64	20	45	6.7	1.7 : 1.0 : 0.23	520
UAXDC3	51	16	40	14	1.0 : 1.0 : 0.23	400
UAXDC4	76	32	45	3.1	1.0 : 1.0 : 0.36	540

4.2.4 Curing of Sample UAXDC1C13

Inside a 2” x 2”, 2 millinch (mil) thick PTFE shim is placed 0.41 g of UAXDC1. To either side of the PTFE shim is placed a sheet of PTFE film (to prevent sticking of the membrane) and a stainless steel plate. This setup is placed inside a Carver® hot press and heated to 160 ˚C before adding 10,000 pounds of pressure for 30 minutes. The heat is reduced to 80 ˚C and the pressure removed before the PTFE film is quickly removed from both sides of the membrane. To each side of the membrane is added 12.5 mg of $SnPh_4$ which is evenly dispersed using a paintbrush. The membrane and shim are again placed between the PTFE film and metal plates and placed into a preheated Carver® hot press at 190 ˚C and 5000 pounds for 48 hours. After this time the temperature is slowly reduced to form a more crystalline material and the pressure is removed after the temperature is below 60 ˚C. Workup is performed according to Example 4.2.10 and properties of the cured membranes are shown in Table 4.5.

ATR-FTIR Analysis (cm^{-1}): 1556 (w); 1467 (s); 1323 (w); 1184 (s); 1143 (s); 1036 (w); 984 (w). Absence of a peak at 2268 (nitrile) and addition of a peak at 1556 (triazine) shows nearly quantitative curing.

4.2.5 Curing of Sample UAXDC2C4

Using the setup from Example 4.2.4, approximately 350 mg of UAXDC2 is placed inside a 2” x 2”, 2 mil thick stainless steel shim. The material is heated to 160 ˚C and 10,000 pounds of pressure is applied before slow cooling and removing the PTFE film from each side of the membrane. To each side of the membrane, 17 mg of $SnPh_4$ is evenly painted on with a paintbrush before placing the membrane between the PTFE films again and heating to 180 ˚C with 4000 pounds pressure for 60 hours before slow cooling. Workup is performed according to Example 4.2.10 and properties of the cured membranes are shown in Table 4.5.

4.2.6 Curing of Sample UAXDC2C6

Using the setup from Example 4.2.4, 0.7440 g of UAXDC2 is placed inside a 2" x 2", 4 mil thick stainless steel shim. The material is heated to 160 ˚C and 10,000 pounds of pressure is applied before slow cooling and removing the PTFE film from each side of the membrane. To each side of the membrane, 30 mg of $SnPh_4$ is evenly painted on with a paintbrush before placing the membrane between the PTFE films again and heating to 190 ˚C under 9000 pounds pressure for 60 hours before slow cooling. Hydrolysis and acidification are performed as described in Example 4.2.11, yielding a swollen membrane approximately 4" x 4" in area, much larger than the original size of the membrane. Drying in a desiccator at 40 ˚C overnight produces a membrane that is still 4" x 4" in area but much thinner than the original material.

4.2.7 Impregnation and Curing of Sample UAXDC2eP1

Two 3" x 3" 1 mil thick membranes of UAXDC2 are formed using a 1 mil PTFE shim between two PTFE films inside a Carver® hot-press at 190 ˚C and 10,000 pounds. The membranes are slowly cooled and removed from the press at 90 ˚C and the PTFE films are quickly removed while the membrane is still hot. To one side of each membrane is applied 30 mg of tetraphenyl tin using a paintbrush to evenly coat the surface. The ionomer membranes are then placed on either side of a 4" x 4" ePTFE sheet with the tetraphenyl tin side of the ionomer membrane in contact with the ePTFE. This setup is placed between two PTFE films and two stainless steel plates before being placed in the preheated Carver® hot-press at 190 ˚C.

The pressure is gently increased to 500 pounds and curing is allowed to proceed for 48 hours before slowly reducing the temperature. Hydrolysis is performed according to Example 4.2.11. Verification of impregnation is performed by visual inspection of the transparentness or opaqueness of the material (where a transparent membrane shows good impregnation) and a scanning electron micrograph (SEM) of a cross-section of the membrane.

Table 4.5. Properties of Cured Terpolymers

Sample	Nitrile : Triazine by IR	Equivalent Weight (g/mol)	Conductivity at 80 ˚C and 20% RH (mS/cm)	Weight Percent Swelling
Nafion 115	n/a	1100	4.7	24
UAXD6 (Ch.2)	n/a	700	15	63
UAXDC1C10	65	640	18	400
UAXDC2C4	63	520	18	-----
UAXDC2C5	200	520	15	-----
UAXDC2C6	150	520	26	420
UAXDC1eP4	-----	-----	15	-----
UAXDC2eP1	100	-----	17	240

4.2.8 Grafted Terpolymer UAXDG1

To refluxing perfluorohexane is added 392 mg of UAXDC1, 126 mg of UAXDHC1, and 28 mg of $SnPh_4$. After dissolving the polymers the heat is removed and the solution is cast onto a petri dish where the solvent is removed via a flow of nitrogen gas at room temperature. The blended polymer is cured similarly to Example 4.2.5 and workup is performed according to Example 4.2.13, yielding a material where the UAXDHC1 is grafted onto the UAXDC1 polymer through the triazine ring.

Table 4.6. Grafted Polymers

UAXDC1 (mg)	UAXDHC1 (mg)	Insoluble Product After Hydrolysis (mg)	Conductivity at 80 ˚C and 20% RH (mS/cm)
175	150	191	10
283	91	343	15
341	82	405	-----
200	0	200	18

4.2.9 MALDI-TOF Mass Spectrometry Analysis

Analysis of the hydrolyzed ammonium sulfonate resin UAXHC4 by MALDI-TOF mass spectrometry is performed using a Bruker Ultraflex TOF instrument by dissolving 20 mg of resin in 1 mL of DI H_2O. An aliquot of 10 microliters of this solution is mixed with 100 microliters of a solution of 7.5 mg/mL 2,5-dihydroxybenzoic acid (DHB) in a DI water containing 0.1 wt% trifluoroacetic acid (TFA). Onto a stainless steel plate is spotted 30 microliters of this final solution, which is allowed to dry before analysis.

4.2.10 IR Spectroscopic Characterization of Cured Membranes

Analysis of the degree of curing is performed by IR spectroscopy. Samples are placed such that the laser shines directly through the membrane. At least three measurements are taken in different portions of the membrane. Disappearance of the peak at 2266 cm^{-1} seen before curing (corresponding to the nitrile) and appearance of the peak at 1556 cm^{-1} (corresponding to the triazine) gives an idea of the degree of conversion from nitrile to triazine.

4.2.11 Hydrolysis and Acidification of Cured Samples

Cured samples are placed in a weight percent solution of 35% DMSO, 15% KOH, and 50% H_2O at 60 ˚C for at least 4 hours. Membranes are then washed with DI water repeatedly until the wash water is neutral by litmus paper. The samples are immersed in 300 mL of DI water and 1.0 M nitric acid is slowly added to acidify the membrane. Partial decantation and addition of 15 M HNO_3 is performed several times until the solution is approximately 15 M HNO_3. This solution is heated to 80 ˚C for 3 hours under a snorkel hood to both dissolve away the tin compounds and any organics present as well as to convert all sulfonates to the acidified form. After the solution is cooled, partial decantation and addition of DI water (note: appropriate safety precautions should be taken when adding water to acid) is repeated five times before complete decantation and water washes are performed until the wash water is neutral. Drying is performed in a desiccator overnight at ambient pressure at 40 ˚C to remove bulk water for easier handling. Fully drying the membranes at high temperatures under vacuum can result in tears, cracks, and imperfections in the membrane making further conductivity and fuel cell testing difficult.

4.2.12 Calculation of Weight Percent Swelling

Membranes that have been soaked in DI water for 1 hour at 20 ˚C are spot dried with a Kimwipe® until bulk dry and weighed. After placing the membranes in a vacuum desiccator at 140 ˚C and 100 torr overnight they are reweighed and the mass loss is used to calculate the weight percent swelling.

4.2.13 Conductivity Measurements

Membrane proton conductivities were measured by United Technologies Corporation at 80 ˚C and various RH conditions using a 4-probe BekkTech conductivity cell (Bekktech LLC, Loveland, CO). Samples are cut into strips (~ 1/3” x 1” size) and mounted in the conductivity cell. The cell is placed in a 25-cm^2 fuel cell fixture (Fuel Cell Technologies Inc., Albuquerque, NM) and a home-made fuel cell test stand is used to maintain the temperature at 80 ˚C during the entire measurement. A purge of 0.25 standard liters per minute N_2 is maintained with desired dew point into the cell for RH controls.

The cell is equilibrated under each RH condition for 30 minutes, then AC impedance measurements are conducted in the frequency range of 100 kHz to 1 Hz using a frequency response analyzer (Solartron 1255B), electrochemical interface (Solartron 1287) and Zplot software (Scribner Associates).

The conductivity is calculated with the below equation, where σ is the membrane conductivity (S•cm^{-1}), L is the distance (cm) between the two voltage sensing electrodes, R is the resistance (Ohm) obtained from the AC impedance measurements, W is the width of the membrane strip, and T is the membrane thickness (cm).

$$\boldsymbol{\sigma = L / (R \times W \times T)}$$

4.2.14 Equivalent Weight Determination

After curing, hydrolysis, acidification, and thoroughly drying the sample at 140 ˚C and 100 torr overnight in a desiccator, approximately 100 mg of the sample is placed in a vial with 35 mL of 0.01 M NaOH and allowed to sit overnight. Three 10 mL aliquots of the solution are taken and back-titrated with a 0.01 M KHP solution. The equivalent weight of the polymer sample can then be determined using the following equation:

$$mL\ NaOH\ consumed = (10\ mL\ NaOH\ - mL\ KHP\ titrant\ ) * \left(\frac{35\ total\ mL}{10\ mL\ aliquot}\right)$$

$$mol\ SO_3H = (mL\ NaOH\ consumed)\left(\frac{1\ L}{1000\ mL}\right)\left(\frac{0.01\ mol\ NaOH}{1\ L}\right)$$

$$Equivalent\ Weight\ = \frac{grams\ polymer}{moles\ SO_3H}$$

4.3 Results and Discussion

4.3.1 Poly(PSEPVE-co-8CNVE) and Poly(Dow-co-8CNVE)

Using the best conditions discovered for homopolymerizing PSEPVE (balancing yield and molecular weight), five room-temperature, bulk polymerizations with a 3P concentration per addition of 5.5 mmol/L are performed with varying amounts of 8CNVE. ATR-FTIR spectra of the materials, as seen in Figure 4.2, are similar to those of poly(PSEPVE) with a new absorbance at 2266 cm^{-1} confirming the presence of nitrile functional groups. ^{19}F NMR spectroscopy of the samples dissolved in R113, as shown in Figure 4.3, allows quantification of the amount of 8CNVE in the polymer by comparing the intensity of the peak at -108.9 ppm, for the CF_2CN group, to the peak at -112.9 ppm, for the CF_2SO_2F functional group. The copolymers prepared, shown in Table 4.1 and 4.2, have 8CNVE contents in the polymer of 5.3 to 20 mol%, similar to the ratio of monomers in the polymerization, suggesting a random copolymerization. One copolymer of Dow and 8CNVE is produced with 17 mol% 8CNVE in the polymer.

Analysis of the hydrolyzed material by MALDI-TOF mass spectrometry is performed similarly to poly(PSEPVE), as discussed in Chapter 3. Peaks seen in the MALDI spectra of the copolymers that are also present in the homopolymer spectra, such as the peak at 1988 m/z seen in Figure 4.4, indicate chains with no 8CNVE incorporation. As the perfluorinated nitrile functional group hydrolyzes in the presence of strong bases to form an amide with a molecular weight of 407 g/mol, peaks shifted down 36 mass units (the difference in molecular weight of the hydrolyzed 8CNVE amide and hydrolyzed PSEPVE) indicate the incorporation of a single 8CNVE monomer in the polymer. Thus, the peak at 1952 m/z in Figure 4.5 indicates polymer chains with 1 8CNVE monomers, while the peaks shifted down 72 mass units at 1916 m/z indicates incorporation of two 8CNVE monomers. Thus, MALDI-TOF MS allows the determination of whether or not individual chains have co-monomer incorporated and their ratios as opposed to bulk measurements such as IR and NMR spectroscopy.

As a greater diversity of chains are present in the copolymer samples than the homopolymer samples, signal-to-noise decreases, and the MALDI data probably mass discriminates towards the lower molecular weights even more. The highest molecular weight peaks clearly seen in the MALDI spectra correspond to 7 monomers per chain. Based upon the amount of 8CNVE monomer in the polymerizations, the ratios of chains containing 0, 1, and 2

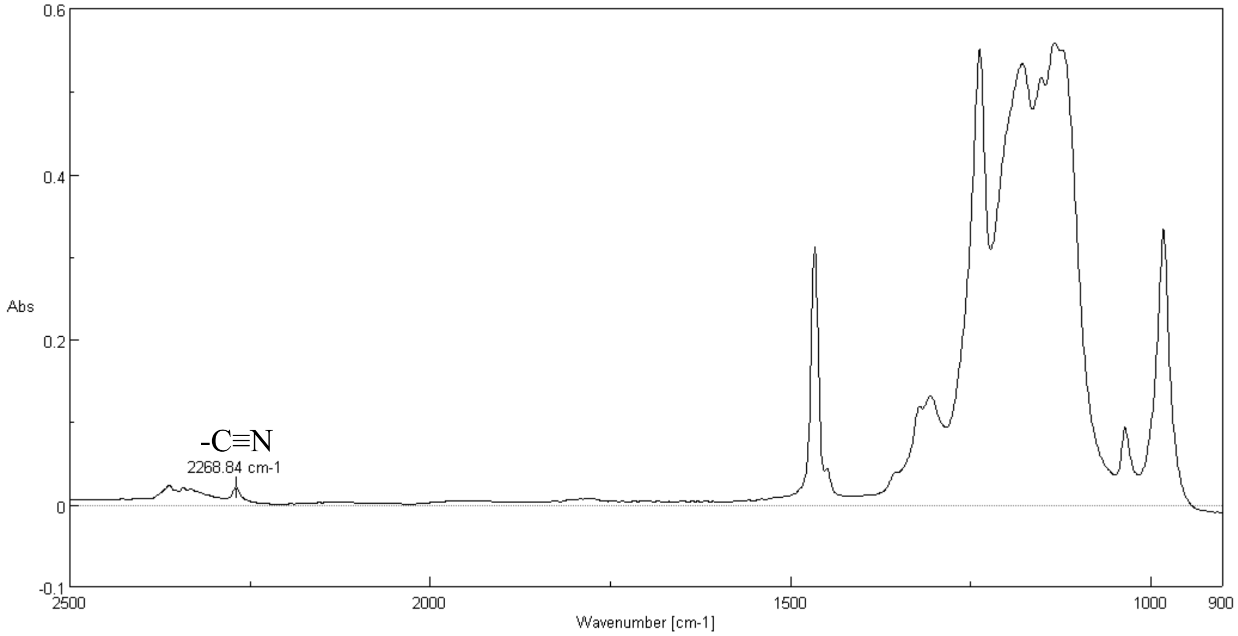

Figure 4.2. UAXHC4 ATR-FTIR spectrum.

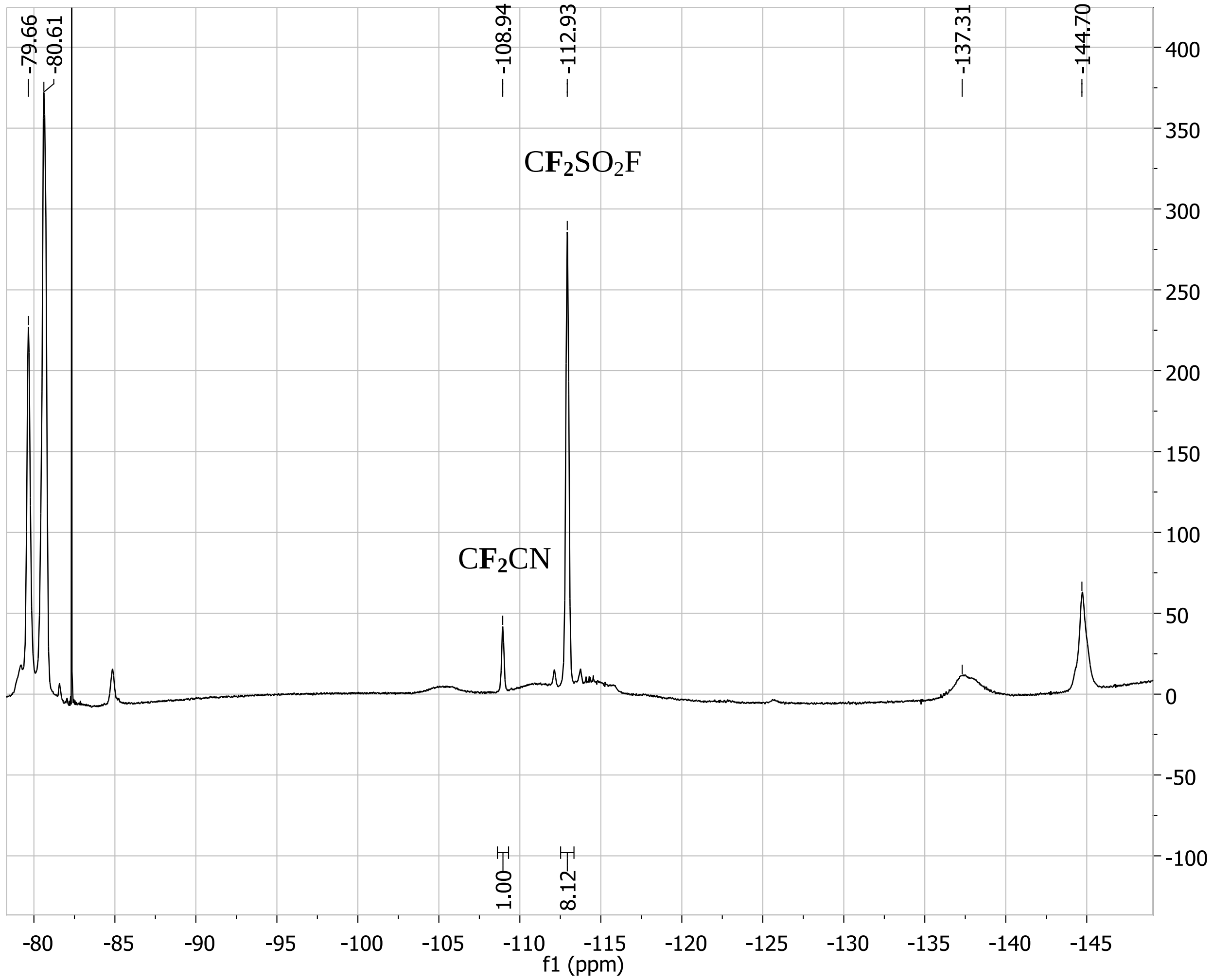

Figure 4.3. ^{19}F NMR spectrum of UAXHC2 dissolved in R113.

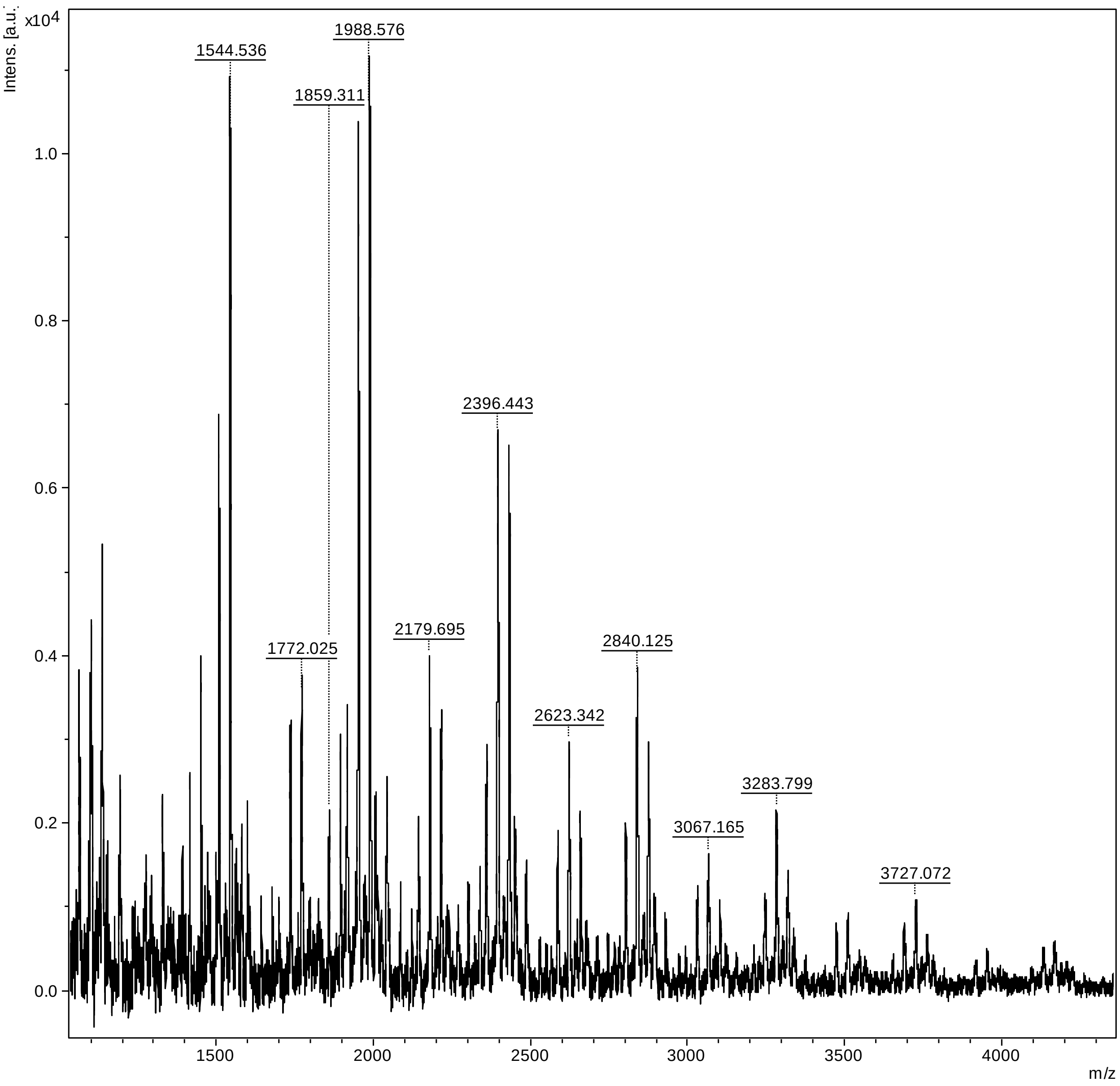

Figure 4.4. UAXHC4 MALDI-TOF mass spectrum.

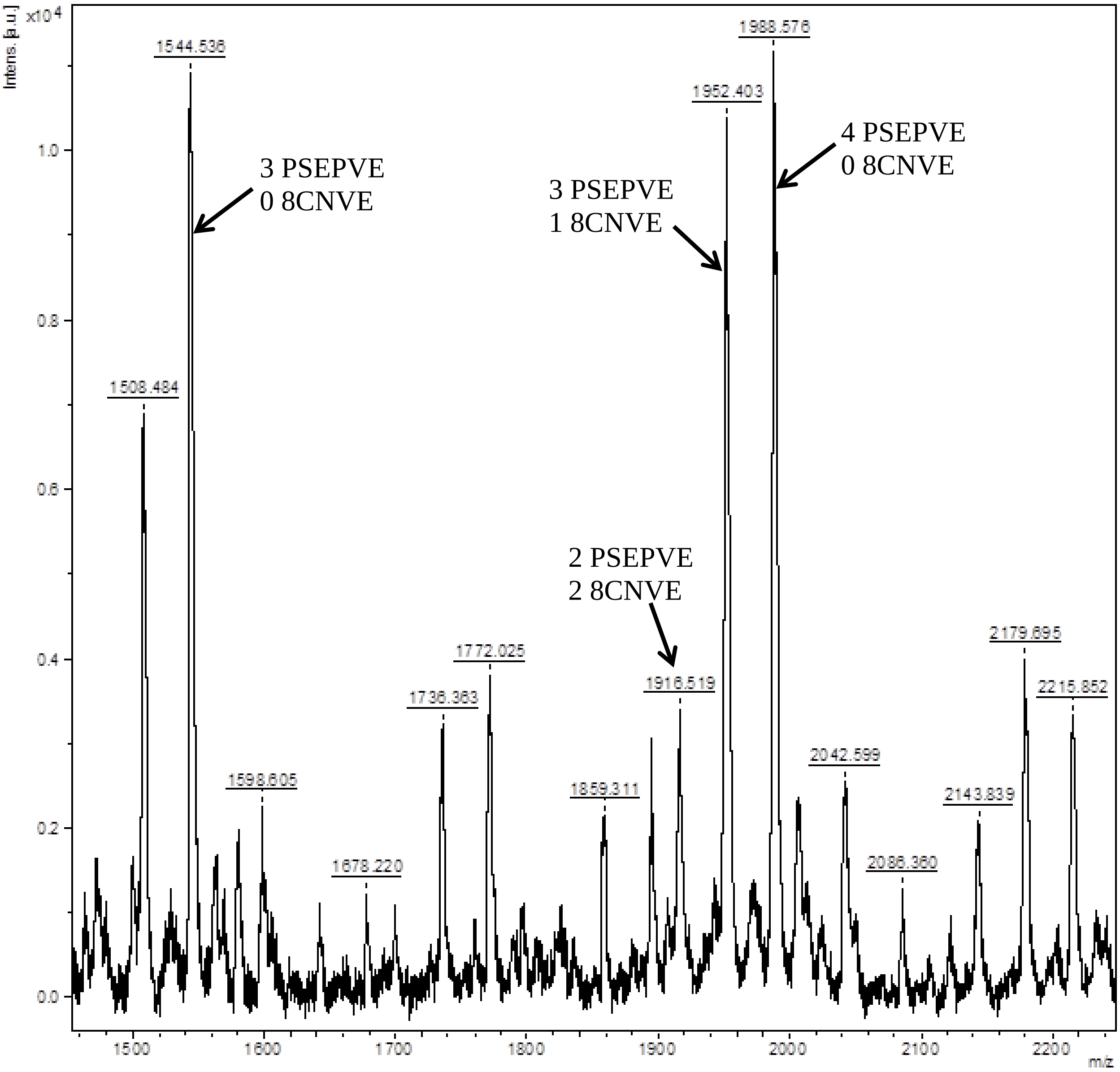

Figure 4.5. Expansion of UAXHC4 MALDI-TOF mass spectrum.

8CNVE monomers appears similar to a Gaussian distribution for such low molecular weight samples, suggesting a random copolymerization. After curing the material becomes brittle with no flexibility, making it difficult to obtain large membranes. However, all cured copolymers of PSEPVE and 8CNVE dissolve in the hydrolysis solution, making them impractical for use in a fuel cell. A higher degree of 8CNVE incorporation into the polymer to obtain a water insoluble material would be illogical as the EWs would increase to values too high to offer any advantage.

As the Dow monomer contains a shorter side chain that is less sterically bulky, it has been hypothesized by the author to be more reactive than PSEPVE and give higher molecular weight polymers. Higher molecular weights are seen in the MALDI-TOF mass spectrum for UAXDH1 shown in Figure 3.21 when compared to UAXH2 shown in Figure 3.13; however, as noted earlier, mass discrimination toward lower molecular weights may be occurring in the MALDI-TOF spectra, suggesting that these are not the true molecular weight distributions. Preparation of a copolymer of Dow and 8CNVE is expected to give a higher molecular weight sample than the copolymers of PSEPVE and 8CNVE, allowing a greater percentage of the polymer chains having one or more 8CNVE monomers with the same molar ratio of the monomers.

Copolymerization of Dow with ca. 15 mol% 8CNVE in solution gives a polymer that contains 18 mol% 8CNVE per polymer chain by ^{19}F NMR spectroscopy of the polymer dissolved in R113 as seen in Figure 4.6. While reactivity ratios cannot be determined from a single polymerization, having a higher degree of 8CNVE in the polymer than in the monomer feed suggests that the reactivity ratio of the Dow vinyl ether in the polymerization is below a value of 1, favoring addition of 8CNVE monomers over the addition of another Dow monomer.

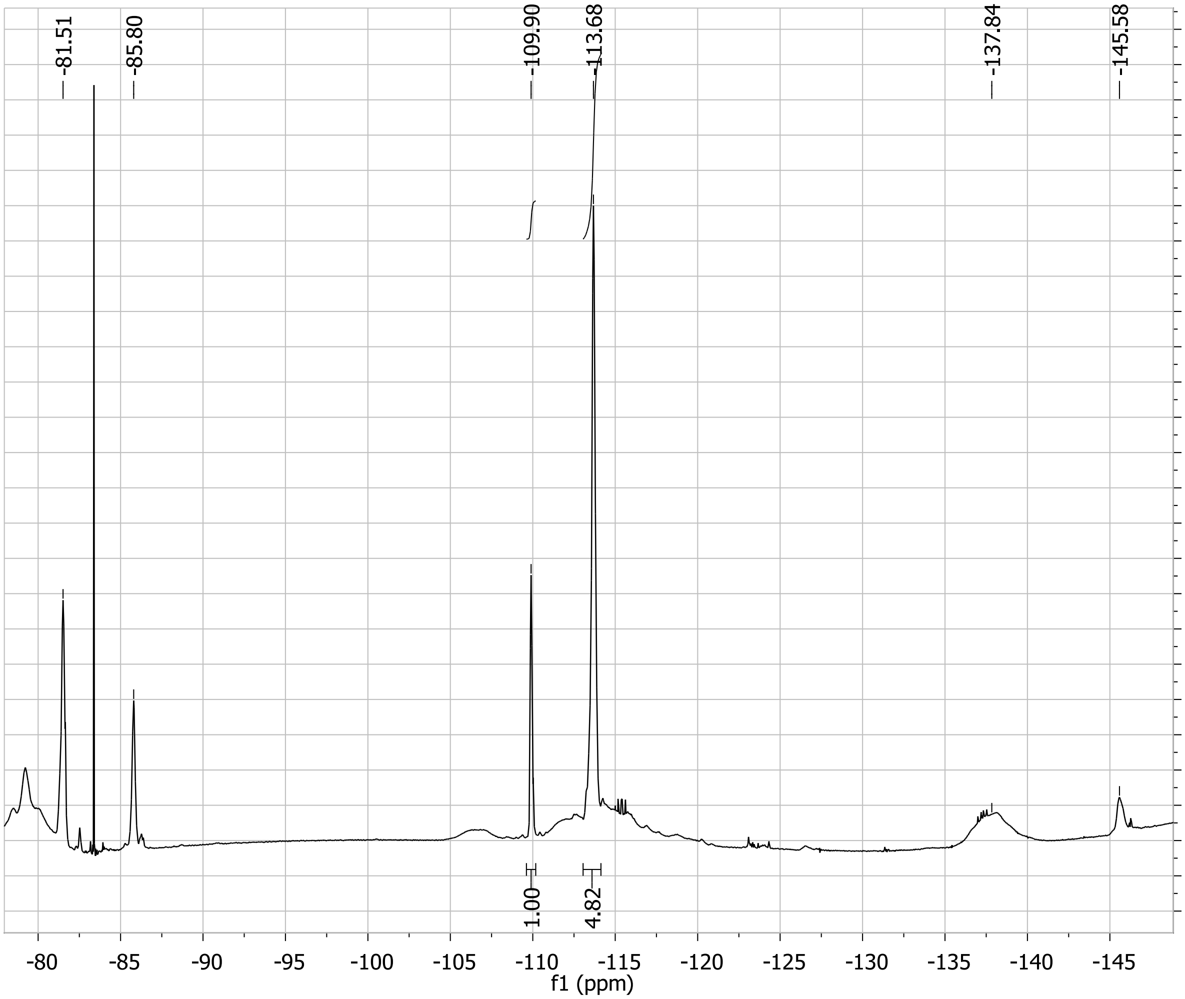

Figure 4.6. ^{19}F NMR spectrum of UAXDHC1 dissolved in R113.

Without GPC measurements and appropriate fluoropolymer standards, the true molecular weight of the sample is not known, making it impossible to know the average number of 8CNVE monomers per chain. Further analysis of the copolymer of Dow and 8CNVE by MALDI-TOF mass spectroscopy again shows a lower molecular weight distribution for the copolymer than the homopolymer due to the increased number of possible chains for the copolymers lowering the signal-to-noise ratio. Signals can be observed up to 5000 m/z, corresponding to roughly 18 monomers per chain, but only clearly to 4000 m/z (see Figure 4.7). An expansion of the MALDI-TOF spectrum (see Figure 4.8) shows only a small peak at 3048 m/z, which corresponds to polymer chains with 11 Dow monomers and no 8CNVE. More intense peaks are seen for polymer chains containing 1, 2, and 3 8CNVE monomers at 3178 m/z, 3307 m/z, and 3437 m/z, respectively. Thus, while it is hypothesized that a higher molecular weight distribution may be present than is seen in the MALDI-TOF spectrum, a sufficient amount of 8CNVE is present in the polymer even if this hypothesis is incorrect.

After curing, a ratio of triazine to nitrile of roughly 80 : 1 can be seen by IR spectroscopy suggesting a high degree of crosslinking. However, the polymer still remains soluble in the hydrolysis solution suggesting it has not been completely networked. It is hypothesized that a high degree of intramolecular crosslinking of the polymer chains may be occurring, which does not increase the molecular weight of the sample, resulting in the material remaining water soluble. Thus, it was decided that TFE must be added to the polymer to increase the molecular weights of the chains before curing, allowing less 8CNVE to be added into the polymer as well as lowering the chances of intramolecular crosslinking.

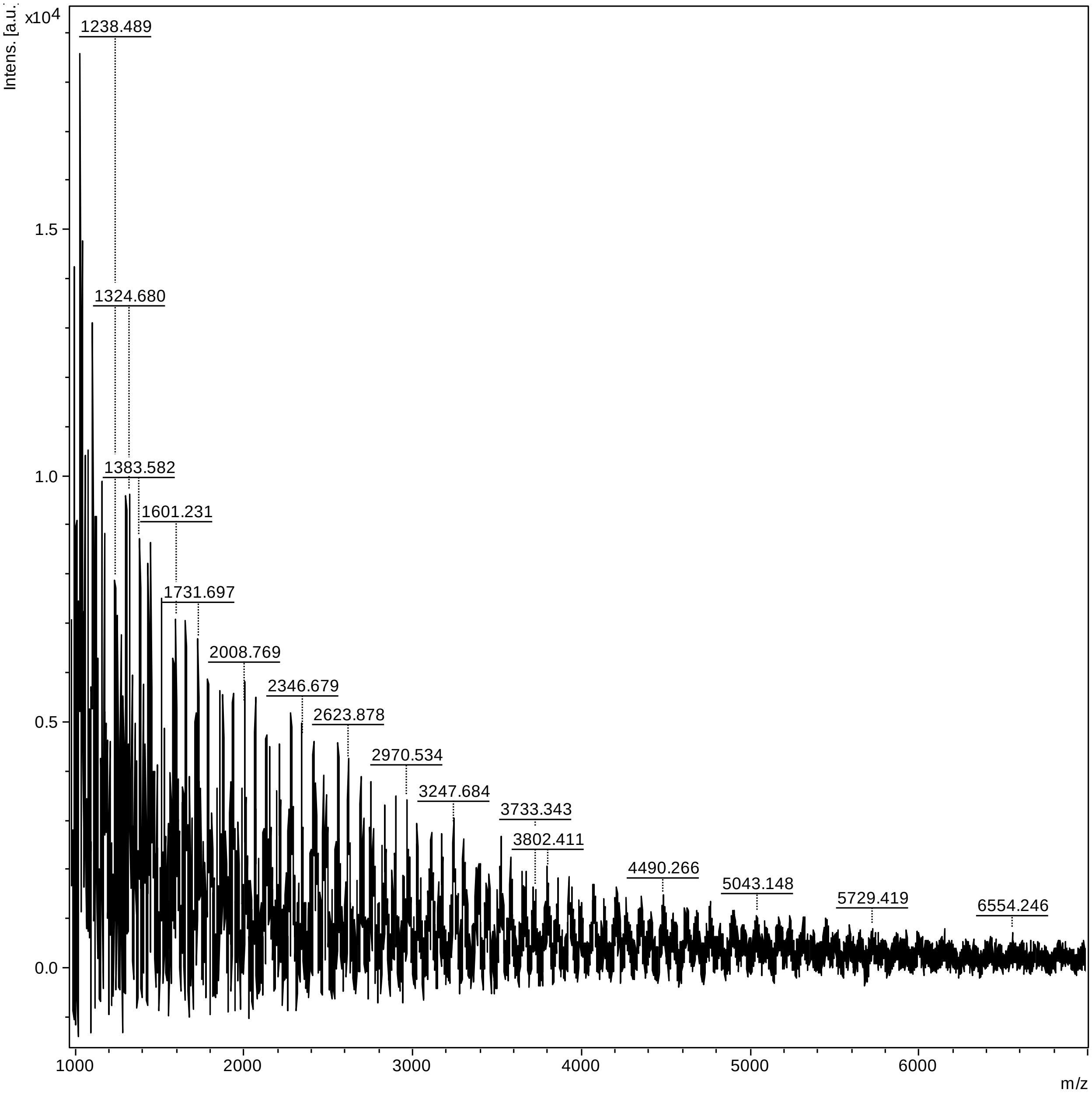

Figure 4.7. UAXDHC1 MALDI-TOF mass spectrum.

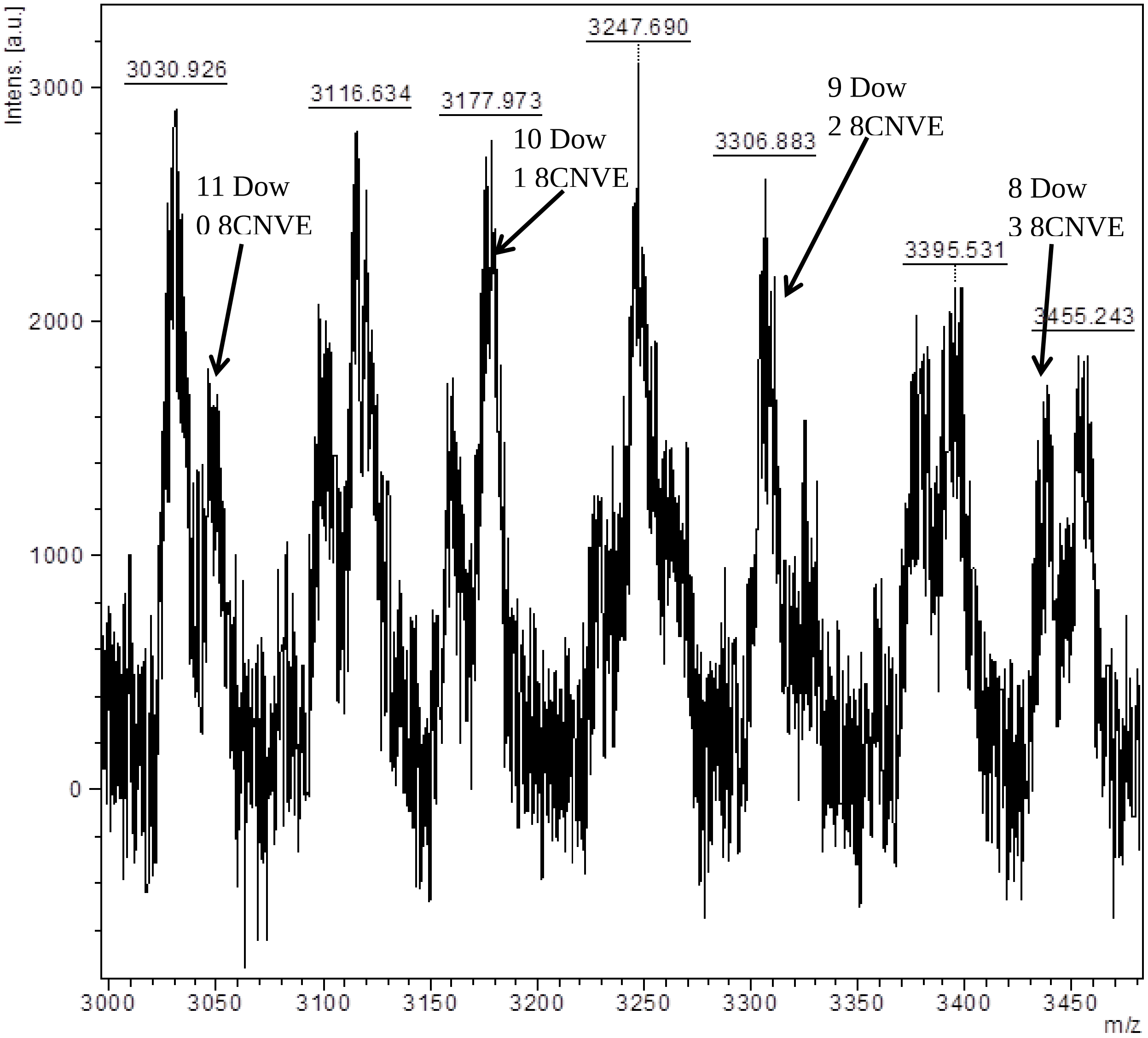

Figure 4.8. Expansion of UAXDHC1 MALDI-TOF mass spectrum.

4.3.2 Poly(TFE-ter-Dow-ter-8CNVE)

To increase molecular weights of the materials, four terpolymers of TFE, Dow, and 8CNVE are prepared using the TFE polymerization system described in Chapter 1. Dow monomer is used as opposed to PSEPVE as it is expected to be more reactive due to the less bulky side group as well as allowing lower EW materials to be prepared with the same amount of TFE. The samples are prepared to have less than 4 : 1 moles of TFE to Dow such that the polymers are water soluble before curing. Carbon dioxide is removed from the TFE feed using the water cooled Ascarite II® scrubber to better control the amount of TFE added during the polymerization. As expected with these low TFE contents, all four samples are indeed water soluble after hydrolysis without curing.

ATR-FTIR spectra show both sulfonyl fluoride and nitrile functional groups present within the polymer, as shown in Figures 4.9-4.12. ^{19}F NMR spectroscopy of the samples dissolved in 1,1,2-trichloro-1,2,2-trifluoroethane (R113), seen in Figure 4.13 and 4.14, allows for the determination of the ratio of Dow to 8CNVE in the polymers by comparing the integrals for the $C\mathbf{F_2}CN$ (-108.9 ppm) and $C\mathbf{F_2}SO_2$ (-112.9 ppm) functional groups of the two repeat units. Of note is that all four samples have a higher mol% 8CNVE in the polymer than the mol% 8CNVE monomer used in the polymerizations, similar to the copolymerization of Dow and 8CNVE, again suggesting the reactivity ratio of Dow with 8CNVE is below a value of 1. Rigorous determination of reactivity ratios for a terpolymer requires more polymerizations than have been performed here, as there are a total of nine possible propagation reactions that can occur.

Determination of the molar ratio of TFE : Dow is more difficult by NMR spectroscopy due to the CF_2 groups having varying chemical shifts. ^{19}F NMR spectrum of poly(PSEPVE) dissolved in R113 (presented in Chapter 3) shows the CF_2 group in the backbone of the polymer

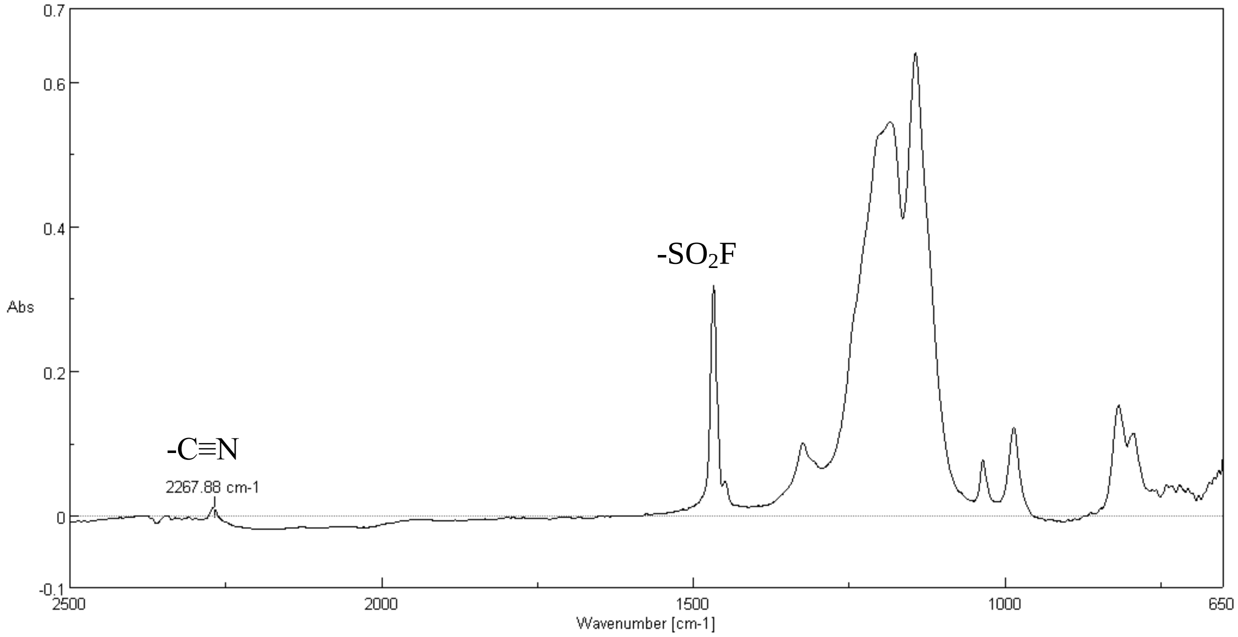

Figure 4.9. UAXDC1 ATR-FTIR spectrum.

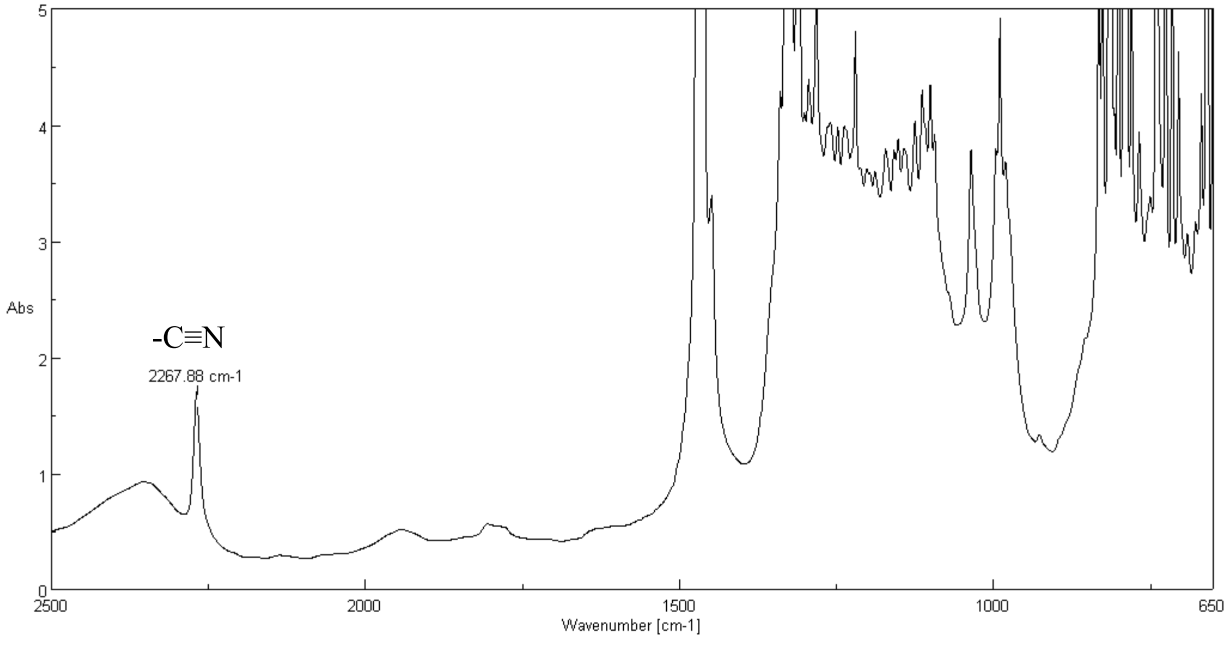

Figure 4.10. UAXDC1 transmission FTIR spectrum.

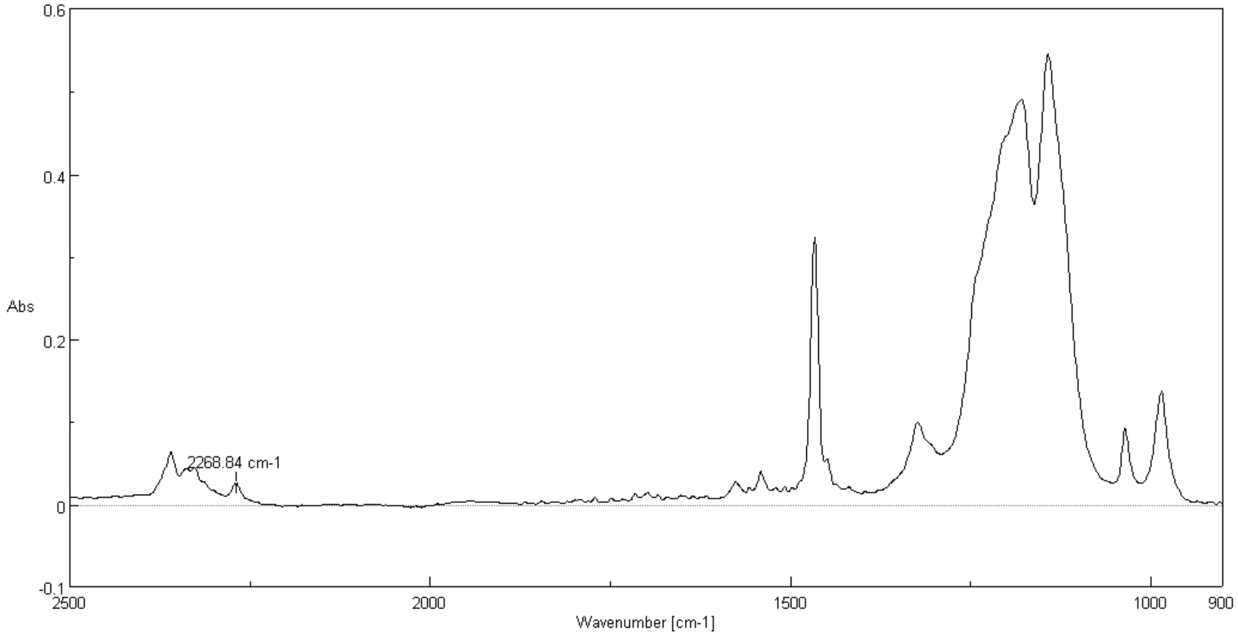

Figure 4.11. UAXDC2 ATR-FTIR spectrum.

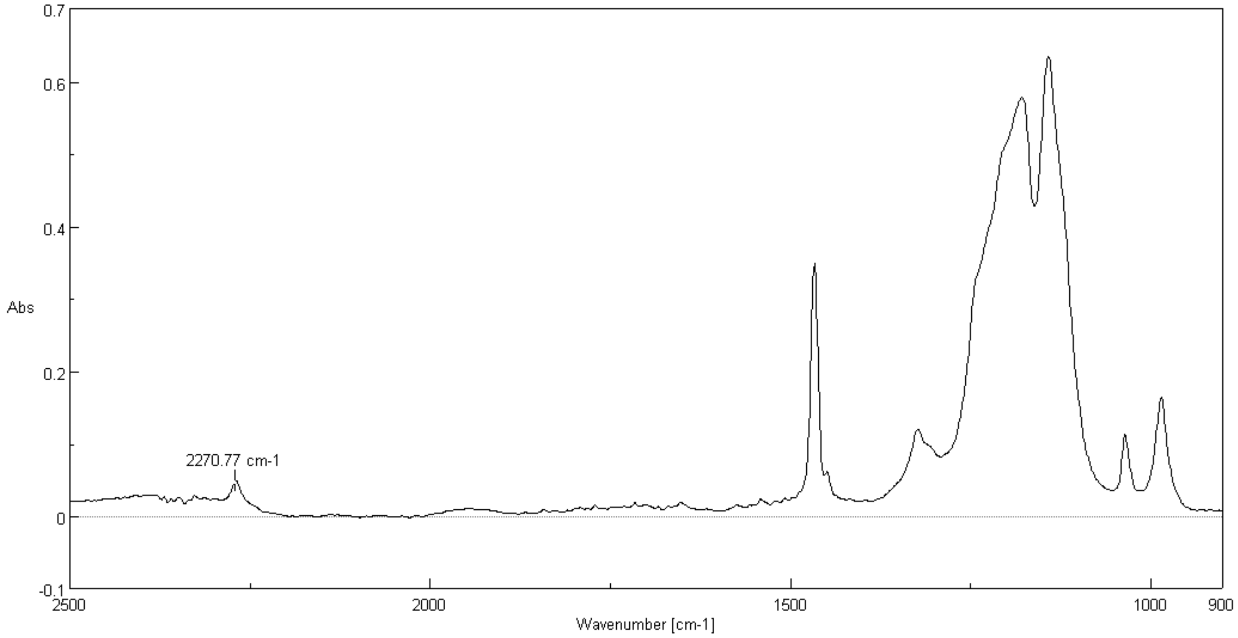

Figure 4.12. UAXDC3 ATR-FTIR spectrum.

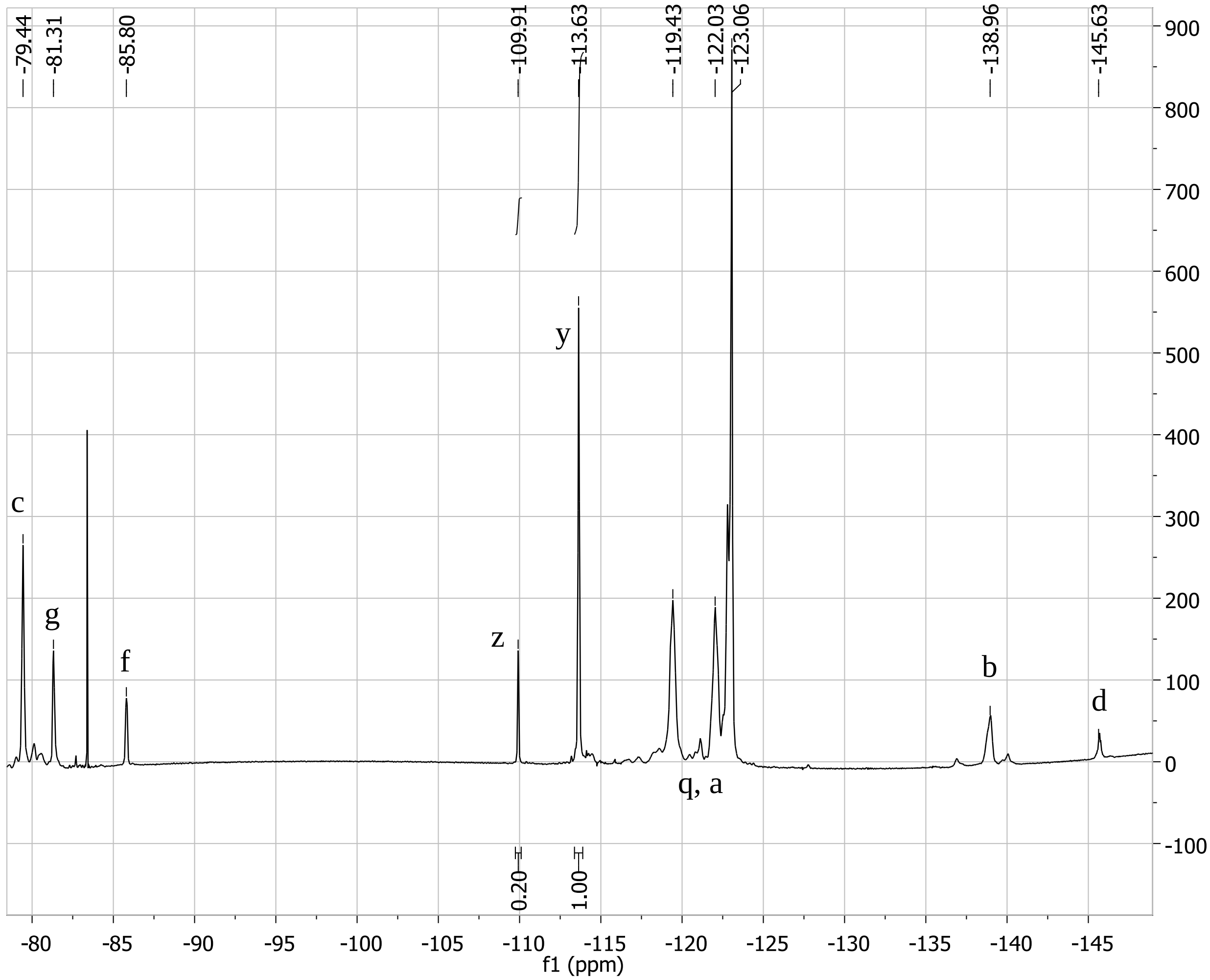

Figure 4.13. ^{19}F NMR spectrum of UAXDC1 dissolved in R113.

$$\{CF_2^aCF^b[OCF_2^cCF_2^ySO_2F^h]\}_n\{CF_2^aCF^b[OCF_2^cCF^d(CF_3^e)OCF_2^fCF_2^zCN]\}_m\{CF_2^qCF_2^q\}_p$$

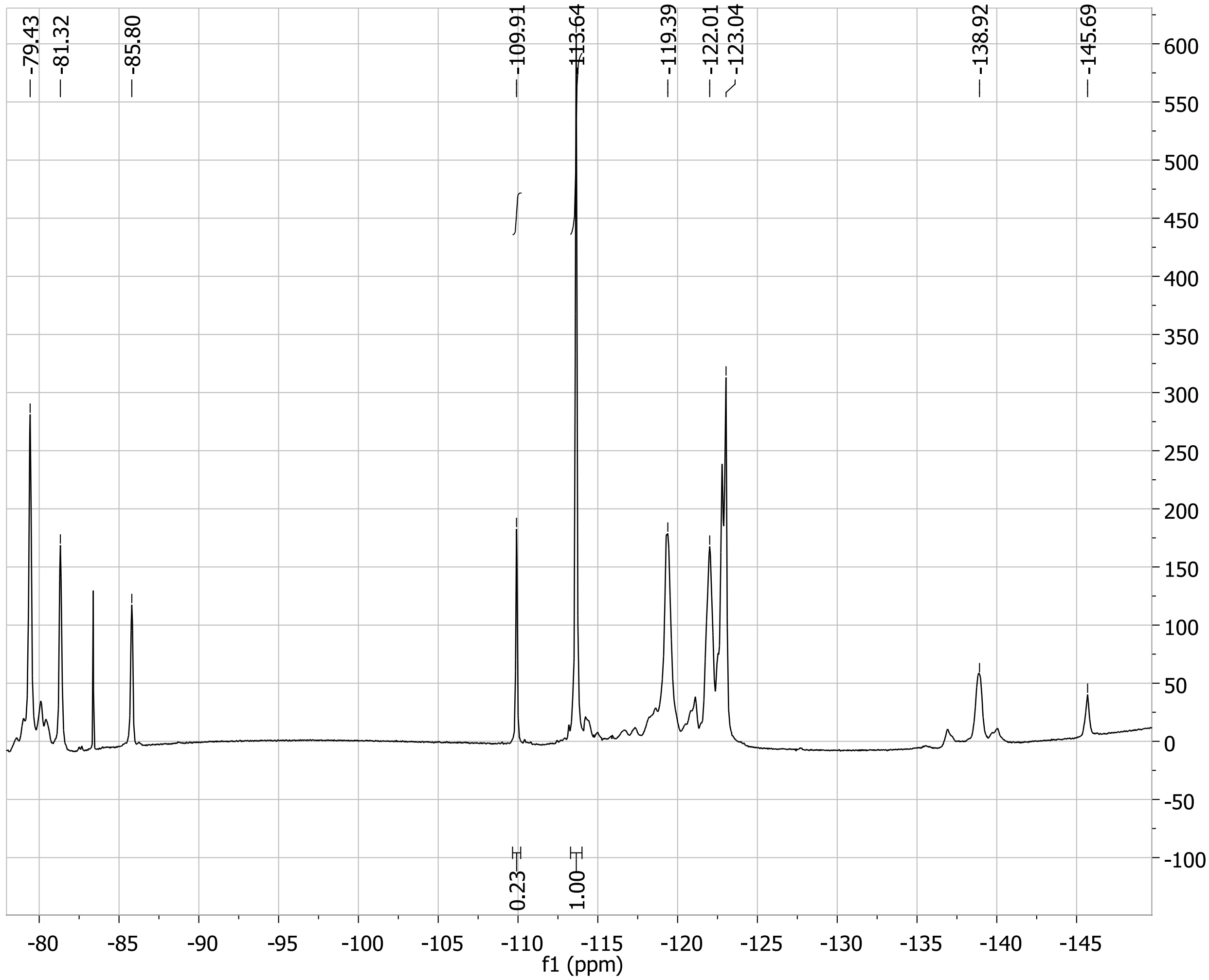

Figure 4.14. ^{19}F NMR spectrum of UAXDC2 dissolved in R113.

to be extremely broad, and if often appears to be hidden in the baseline. This broadening is likely due to the two bulky groups on either side preventing free rotation. However, with just one PSEPVE unit beside the CF_2 group, it may sharpen up and give rise to one of the peaks seen between -119 and -124 ppm in Figures 4.13 and 4.14, but it is difficult to accurately assign each of these peaks and know the exact structure of the backbone in the random terpolymer. Thus, EWs are determined by back titration with 0.01 M sodium hydroxide and KHP standards. Determination of the amount of TFE in the polymer is accomplished by taking the ratio of Dow : 8CNVE from ^{19}F-NMR spectroscopy and back-calculating the amount of TFE present in the polymer to obtain the EW measured by titration. As no titrations of sample UAXDC4 could be performed as the material is water soluble, the EW is estimated by ^{19}F-NMR spectroscopy and compared to the values obtained for UAXDC1-3.

Using these results, it can be seen that a change of just 5 psi of TFE pressure during the polymerization has a large impact on the amount of TFE in the terpolymers at these low EWs. Increasing the pressure of neat TFE from 40 psig to 45 psig changes the ratio of TFE : Dow from 1.0 : 1.0 to 1.7 : 1.0. Again increasing the pressure of TFE by another 5 psig increases the ratio of TFE to vinyl ether in the polymer to 3.0 : 1.0. Increasing the amount of TFE in the polymers also increases the yield due to molecular weights increasing as the polymerization is less TFE starved. Sample 4 from Table 4.4 has an increased ratio of 8CNVE to Dow that likely contributes to the increased yield of polymer as it has been shown the reactivity ratio of Dow is below a value of 1, likely increasing molecular weights with more 8CNVE in the monomer feed.

Some current methods for curing perfluoroalkyl nitriles to triazines involve addition of an amine that decomposes to ammonia at the elevated temperatures used in the curing step, which helps to increase the rate of trimerization.[6a] However, this route cannot be used for these polymers as the generation of ammonia would also produce a large amount of sulfonamide functional groups, which show little proton conductivity and cannot be readily converted back to sulfonic acid groups. While curing times are quite long (over 24 hours), little work is done here to improve the rate and likely a large amount of work has already been performed by DuPont on increasing the rate of curing, and if so, this information has been kept as a trade secret.

The ideal conditions to give high conversion of nitrile to triazine are found to be 190 ˚C with at least 5000 pounds pressure and two days of curing time. Of additional importance is ensuring adequate coverage of the $SnPh_4$ over the surface of the membrane. Since the reaction takes place in the solid state the two compounds must be intimately mixed to react to completion. Using a small paintbrush purchased from an arts and crafts supply store, it has been found the tetraphenyl tin could be well dispersed on the surface of the membrane allowing the high curing temperature to melt the polymer and high pressure to force the tin into the polymer matrix. Analysis of the pre-cured and post-cured membranes by IR spectroscopy, by comparing the intensity of the peak at 2270 cm^{-1} (nitrile) to the peak at 1556 cm^{-1} (triazine) for Figures 4.15-4.18, shows nearly quantitative conversion of nitrile to triazine.

Hydrolysis is performed using similar conditions as those employed by DuPont for the hydrolysis of Nafion® except at 60 ˚C instead of 80 ˚C.[9] Once hydrolysis begins the materials show a high degree of swelling, making complete hydrolysis much easier than with more crystalline, high EW polymers. After hydrolysis, water washes are performed until all of the excess KOH is removed, which is verified by testing the basicity of the decanted solution using litmus paper. Acidification is performed slowly, as quickly adding concentrated nitric acid causes the membranes to rapidly shrink and tear. Also, pouring dilute nitric acid on just one portion of the membrane again causes contraction of that one portion of the membrane and leads

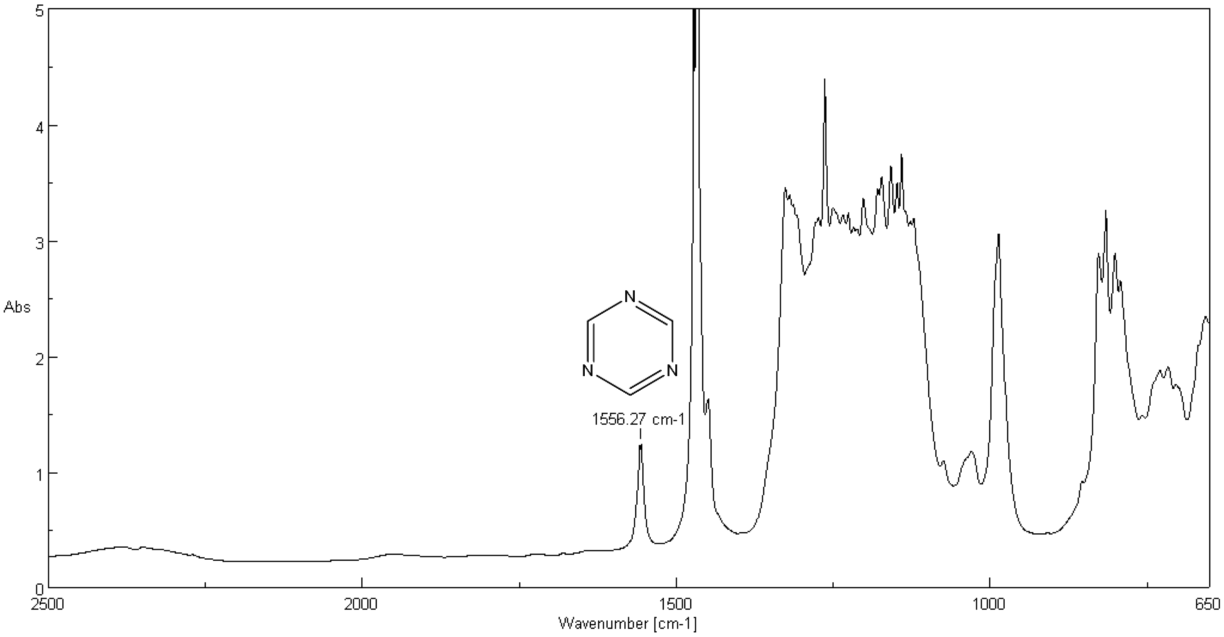

Figure 4.15. UAXDC1C14 transmission FTIR spectrum.

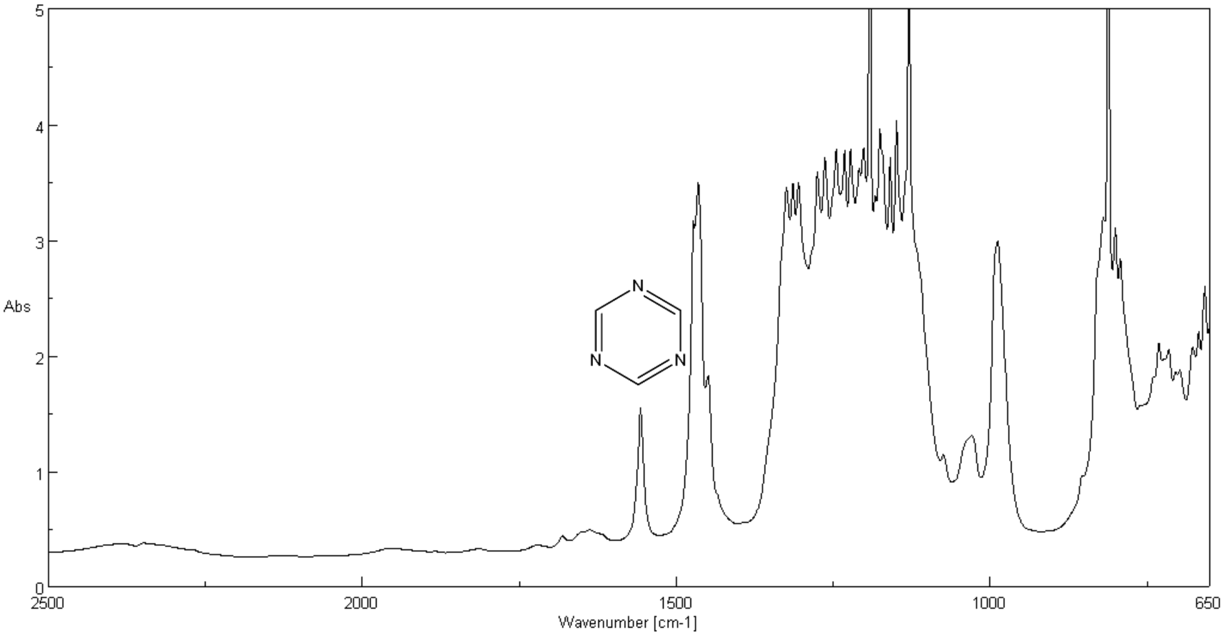

Figure 4.16. UAXDC2C5 transmission FTIR spectrum.

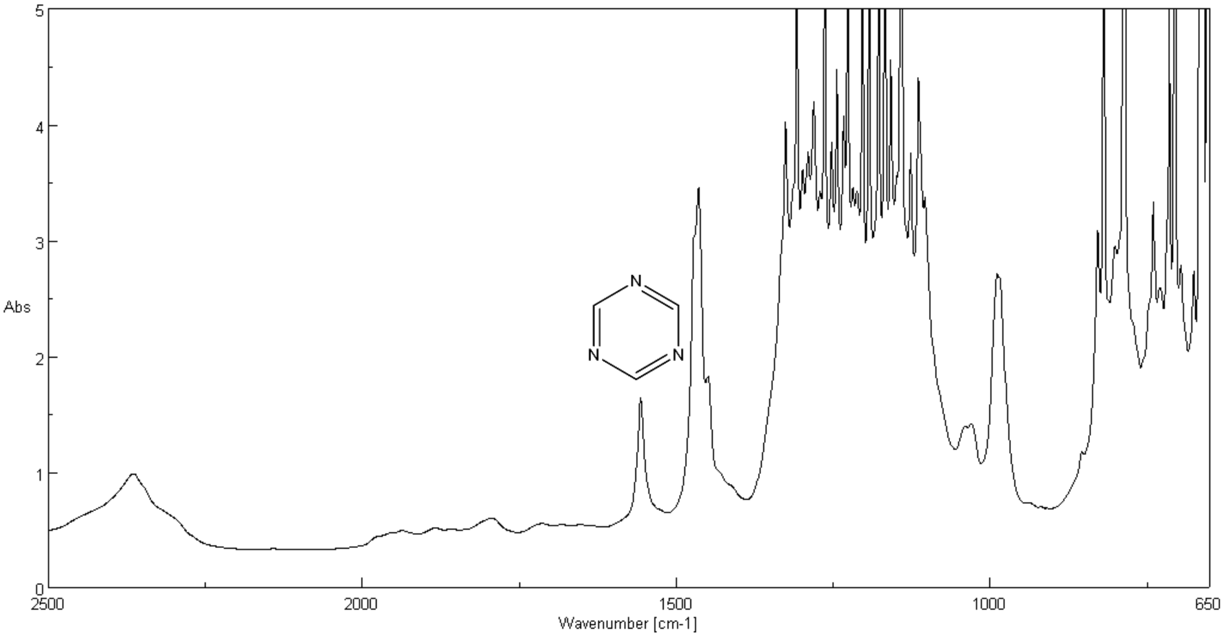

Figure 4.17. UAXDC3C4 transmission FTIR spectrum.

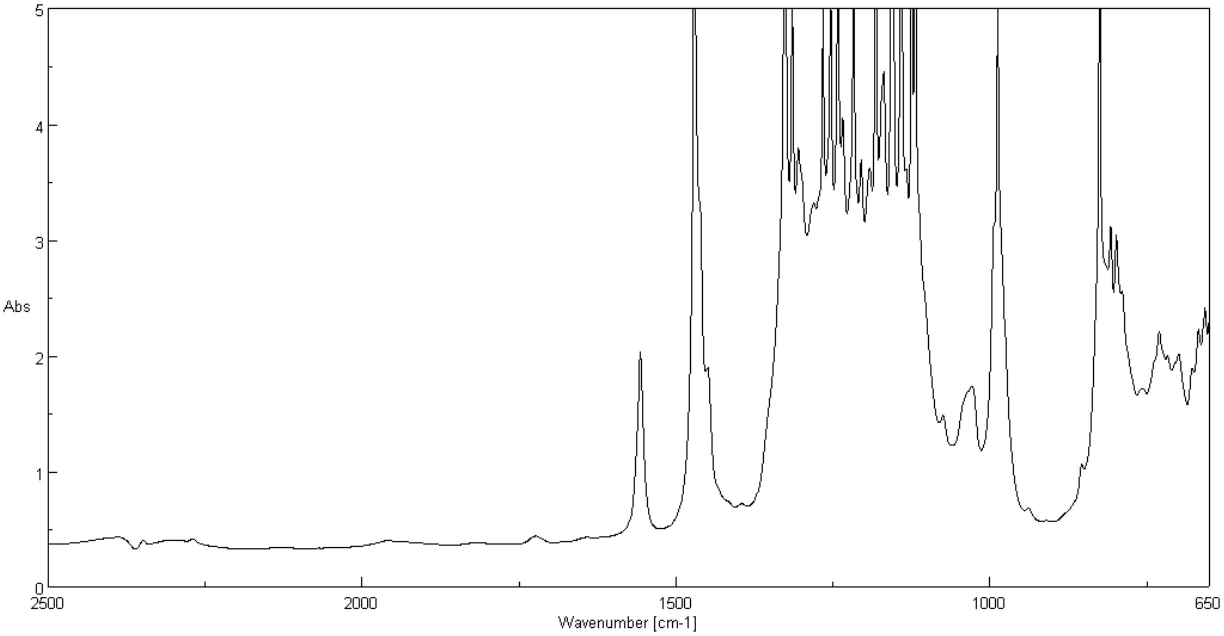

Figure 4.18. UAXDC4C2 transmission FTIR spectrum.

to tearing. Thus, the membranes are immersed in water and a dilute solution of nitric acid is added to the water to allow slow diffusion of the nitric acid to the entire membrane. Partial decantation followed by addition of small amounts of concentrated nitric acid allows the concentration of nitric acid to be slowly increased without destruction of the membrane. Once this has been performed several times such that the solution is close to 15 M HNO_3, it is heated to 80 ˚C under a snorkel hood to dissolve and remove any remaining tin compounds and clean the membrane of any organic molecules present. Slow drying in a desiccator is done to prevent the materials from warping and shrinking or stretching during the drying process.

Proton conductivities of sample UAXDC1 are in reasonable agreement with the expected results. Well cured UAXDC1 samples that did not have any imperfections in the membrane typically had conductivities around 14 - 18 millisiemens per cm (mS/cm) at 80 ˚C and 20% relative humidity, compared to 4.7 mS/cm for Nafion® 115 and 15 mS/cm for sample UAXD6 prepared in Chapter 2. With an EW of 640 g/mol for sample UAXDC1 and 700 g/mol for UAXD6, it is seen the slightly lower EW sample shows to have a slightly higher conductivity as would be expected. No significant increase or decrease in conductivity is seen between the samples UAXDC1 and UAXD6, where both samples have similar EWs, but the sample UAXDC1 is crosslinked and has the additional triazine functional group present. This suggests conductivities are not drastically altered by the addition of the triazine crosslinks.

Literature reports show that TFE and Dow copolymers with EWs from 650 to 770 g/mol do not show an increasing trend in conductivity with lowered EW.[10] The paper attributes this to a "frustrated network" suggesting the sulfonic acid clusters cannot properly form channels due to the shorter side chain having less flexibility. Here, three well cured samples of UAXDC2 that are prepared similarly to Example 4.2.6 show conductivities between 15 and 18 mS/cm. Thus, no gain in conductivity is seen using these membrane preparation conditions despite decreasing the EW from 640 to 520 g/mol.

Preparation of a 4 mil thick membrane as opposed to a 2 mil thick membrane is performed by simply using a 2” x 2”, 4 mil thick shim. After hydrolysis, acidification, and drying in a desiccator at 40 ˚C overnight, the membrane swells in the x-y direction while becoming thinner such that it is now 4” x 4” and 1-2 mils thick. AC Impedance spectroscopy of this material shows a conductivity of 26 mS/cm, significantly higher than the two previous materials. It thus appears that by taking a thick, swollen membrane and slowly drying, the frustrated network effect can be removed to yield more conductive materials.

By having a highly swollen membrane and then slowly drying, the polymer chains and side chains can orient themselves such that the frustrated network phenomenon is removed. The typical condition used for forming membranes here is to crosslink the polymer chains into a 2 mil thick membrane, then after hydrolysis, acidification, and drying a 2 mil thick membrane is prepared. Using this route, a 4 mil thick membrane is cured which after hydrolysis, acidification, and drying becomes around 1-2 mils thick. This thinning of the membrane may allow for the polymer chains to re-orient themselves to form better sulfonic acid channels through the membrane and increase the proton conductivity. This workup method should be further investigated to see if conductivities can be increased even higher through better membrane processing techniques.

Sample UAXDC3 with a TFE : Dow molar ratio of 1 : 1 is found to still be soluble in the hydrolysis solution despite near quantitative curing by IR spectroscopy. Sample UAXDC4 is prepared with an increased amount of 8CNVE in the polymer, having a ratio of 1 Dow to 0.36 8CNVE to see if the increased amount of curing agent would yield a water insoluble material with these low TFE contents. After curing and hydrolysis the material is shown to be insoluble based upon ^{19}F NMR spectroscopy of the hydrolysis solution. However, the weight percent swelling is over 800%, and no membrane of the material could be prepared that did not lose its form instantly on contact with water, making conductivity measurements impossible.

The conductivities at 80 ˚C and 20% RH of 18 and 26 mS/cm for samples UAXDC1 and UAXDC2 are roughly 3.8 and 5.5 times higher than Nafion® 115. Additionally, the conductivities of the samples are higher than those of the lowest EW water insoluble membranes that can be made from these types of monomers without addition of a cure-site monomer. For example, the polymer with 4 TFE monomers per Dow (sample UAXD6 from Chapter 2) has a conductivity of 15 mS/cm compared to 18 and 26 mS/cm for the terpolymers produced here. However, this increased conductivity comes at some cost as the weight percent swelling of these materials is over 400%, likely too high for operation in a fuel cell. This increased swelling is due to the loss of crystallinity by having such a small amount of TFE with a co-monomer containing a bulky side group. While the entropy of solution for the networked polymer prevents it from dissolving, no change in the enthalpy of solution has been made. Thus, when placed in water the materials show a large degree of swelling, similar to hydrogels.

4.3.3 Impregnation of Terpolymers in ePTFE

In an attempt to minimize swelling of the materials, the new ionomers are impregnated inside ePTFE mats. While porous mats from other polymers are available, such as poly(vinylidene difluoride) (PVDF) and polyethylene (PE), ePTFE is used due to its chemical and thermal stability to withstand both fuel cell conditions and the workup conditions of the membranes, including 60 ˚C KOH and 80 ˚C HNO_3. The mat used has a thickness of 1.5 mils with 90-95%, void space according to DuPont, the manufacturer. Visual inspection of the material shows it to be an opaque white material similar in appearance to virgin PTFE. A 24 cm by 13 cm piece of the material has a weight of 0.3272 g, giving a bulk density of 0.2753 g/mL, well below the density of virgin PTFE at 2.20 g/mL.[11] Scanning electron microscopy (SEM) shows the material to be made of particles with fibrils connecting and holding the agglomerated particles together, as seen in Figure 4.19.

Two methods are possible for impregnating the ionomer inside the mat, solution casting and melt-flow. Solution casting has been attempted with the uncured resin dissolved in fluorinated solvents such as perfluorohexane, HFC-4310, and R113. However, the weight percent solids of these solutions are all below 3%, requiring many castings. Additionally, with the low boiling points of these solvents large amounts of the ionomer simply precipitate on the surface of the ePTFE instead of inside the mat. After several infiltrations of the ionomer inside the ePTFE, it is observed that the surface of the ePTFE is coated in ionomer despite remaining opaque, suggesting poor filling inside the mat. Solution casting the cured and hydrolyzed polymer in a water alcohol mixture, as is commonly done with Nafion®, has not been attempted but is likely a good avenue for future work.

One of the main concerns with the melt-flow impregnation method is the ePTFE mat is compressible and with too much pressure or heat the material will become thinner and lose porosity. The manufacturer’s maximum suggested operating temperature of the material before aggregation of the PTFE particles begins is 180 - 190 ˚C. This means at higher temperatures the ePTFE will likely lose its porosity unless the ionomer melts at these temperatures and can quickly fill the voids, preventing agglomeration of the ePTFE particles. It is found that up to 250 ˚C, sample UAXDC2 does not melt and has no flow unless pressure is applied suggesting

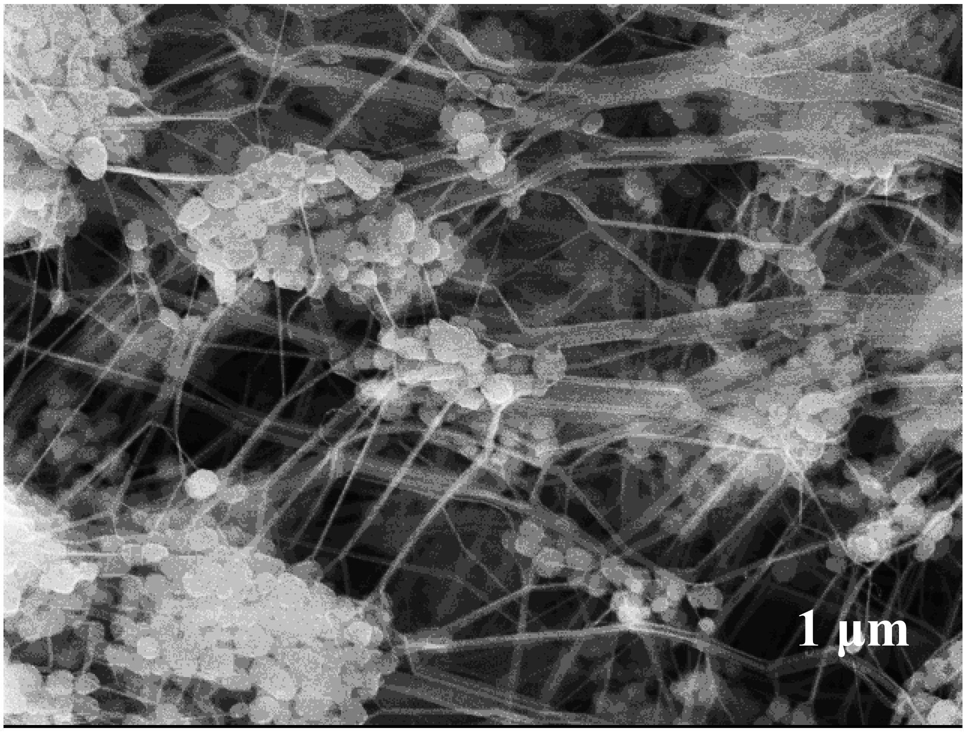

Figure 4.19. SEM image of ePTFE.

the use of high temperature and allowing the polymer to melt into the pores without pressure is not feasible.

The best condition found for impregnation involves pre-pressing two membranes of the ionomer into 1 mil thick membranes that are placed on either side of the ePTFE mat with tetraphenyltin as the catalyst. With just 500 pounds pressure in the hot-press at 190 ˚C, the ionomer can flow into the pores of the ePTFE mat such that the cured composite material no longer appears opaque, as seen in Figure 4.20, but becomes transparent, as seen in Figure 4.21. Poor impregnation of the ePTFE or complete compression of the ePTFE into a thin membrane with ionomer on either side both result in an opaque material. After hydrolysis, acidification, and drying, membranes are found to be more mechanically stable and easier to handle than neat membranes of UAXDC2.

AC impedance measurements of the sample show a drop in the in-plane conductivity, from 26 to 17 mS/cm, as expected based on the addition of non-conductive PTFE to the material. However, the weight percent swelling also dropped from 420% down to 240%, a marked improvement. SEM images of a cross-section of the membrane, seen in Figures 4.22 and 4.23, show that while the mat is well impregnated, it is also compressed from a starting thickness of 35-40 microns to 10 microns. There exists approximately 20 microns of neat ionomer on either side of the mat that is not impregnated. Testing inside a fuel cell shows a hydrogen crossover of 0.9 mA/cm^2 compared to 1.8 mA/cm^2 for Nafion® 112 at 80 ˚C and 30% RH. Additionally, the resistance drops from 0.554 ohm for Nafion® 112 to 0.38 ohm for UAXDC2eP1. Thus, despite the compression of the ePTFE mat, good properties such as reduced swelling, lower hydrogen crossover, and reduced resistances are still seen compared to Nafion®. With better impregnation of the mat by the ionomer it should be possible to see even higher levels of improvement.

Figure 4.20. Visual image of ePTFE mat.

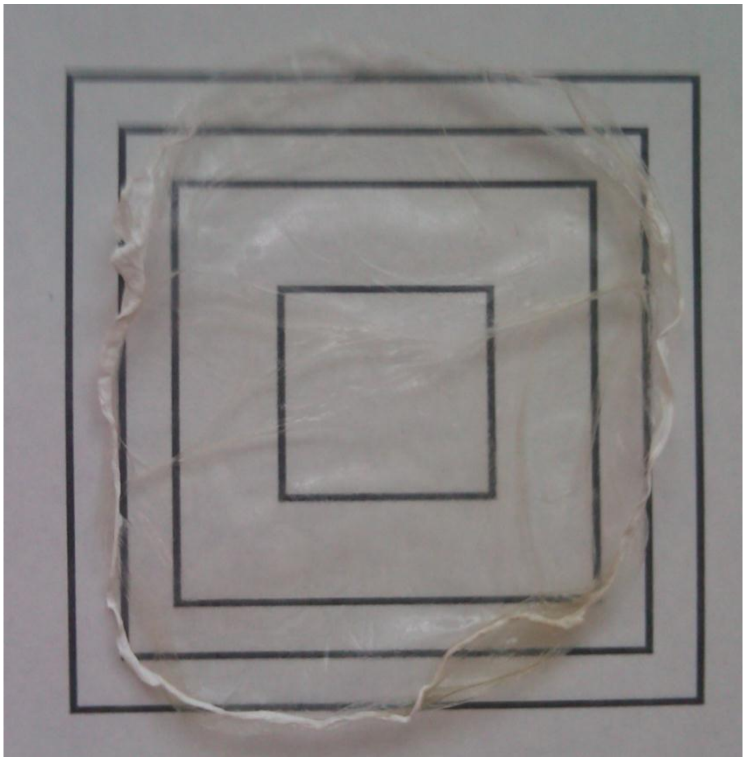

Figure 4.21. Visual image of UAXDC2eP3. Boxes are 1”x1”, 2”x2”, 2.5”x2.5”, and 3”x3”.

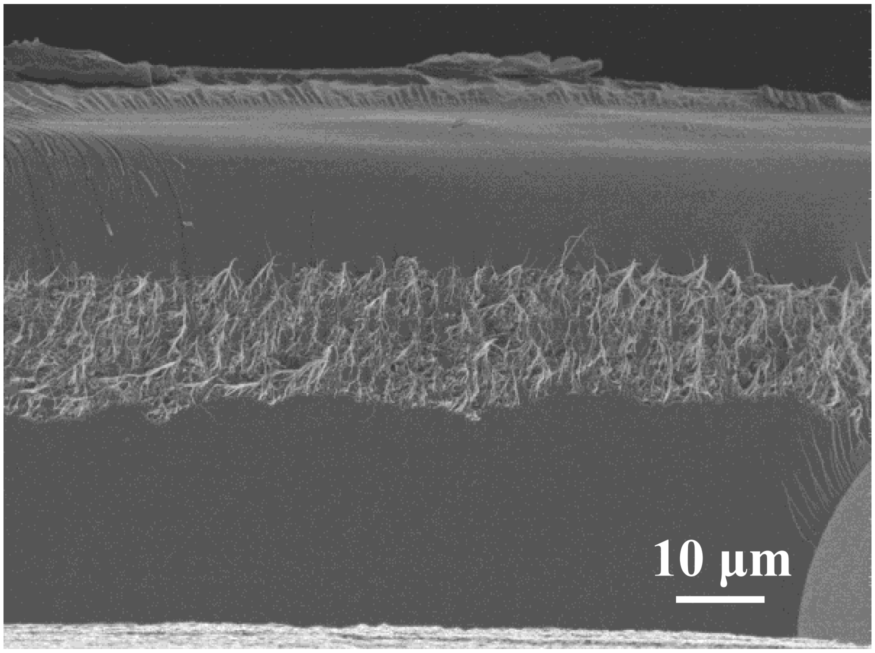

Figure 4.22. SEM image of UAXDC2eP1 cross-section.

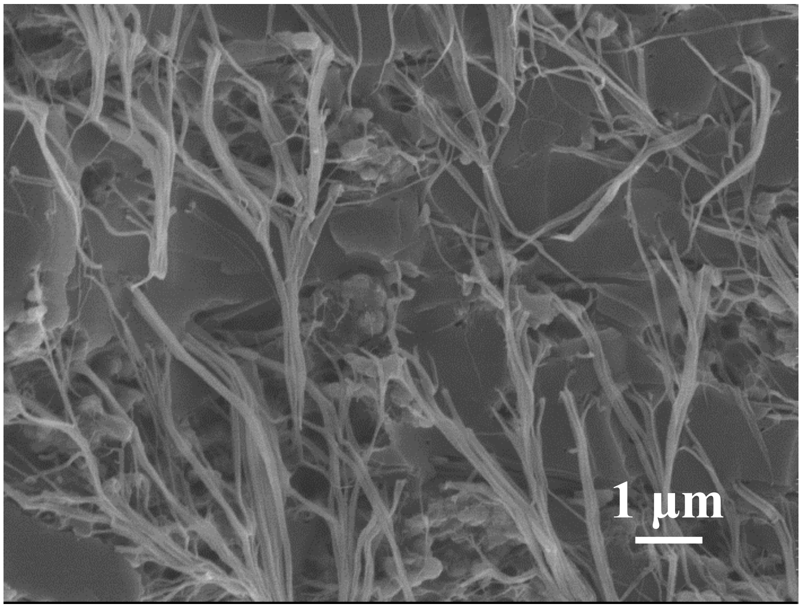

Figure 4.23. Magnified SEM image of UAXDC2eP1 cross-section.

4.3.4 Grafted Polymers

As has been shown by personnel at the 3M Company, taking a water insoluble membrane and increasing the number of acid sites on the side chain can lower the EW while retaining water insolubility and a high degree of crystallinity to keep swelling down.[1] A similar approach could be attempted with these materials by grafting the poly(Dow-co-8CNVE) copolymer onto the poly(TFE-ter-Dow-ter-8CNVE) material through the triazine curing. This method allows for tuning of the EW of the materials without having to prepare new polymers. Additionally, if higher EW samples are used than those prepared on this project in Table 4.4, the increased crystallinity from TFE in the backbone could help reduce swelling while the low EW copolymer allows for a high conductivity.

For this work, the highest EW sample with the best mechanical properties, UAXDC1, is used as the backbone. The copolymer is sample UAXDHC1 that contains 17 mol% 8CNVE. Three different experiments are attempted with varying amounts of the copolymer, as shown in Table 4.6. Sample UAXDCG1 has a high amount of the copolymer, and it was determined that this sample still had a large amount of water soluble material. As cured samples of UAXDHC1 remain water soluble, it is likely that clusters of copolymer formed that do not cure to the UAXDC1 backbone. As the amount of copolymer in the sample decreases and a greater fraction of the copolymer grafts to the terpolymer backbone instead of other copolymers, the fraction of water insoluble product increases. With 20 weight percent copolymer before curing, 96% of the sample remains water insoluble with a high ratio of triazine to nitrile in the IR spectrum shown in Figure 4.24. Despite the lowered EW, conductivity measurements of the samples actually decreased compared to the conductivity of UAXDC1. This decreased conductivity may be due to the “frustrated network” requiring better membrane fabrication methods to be discovered.

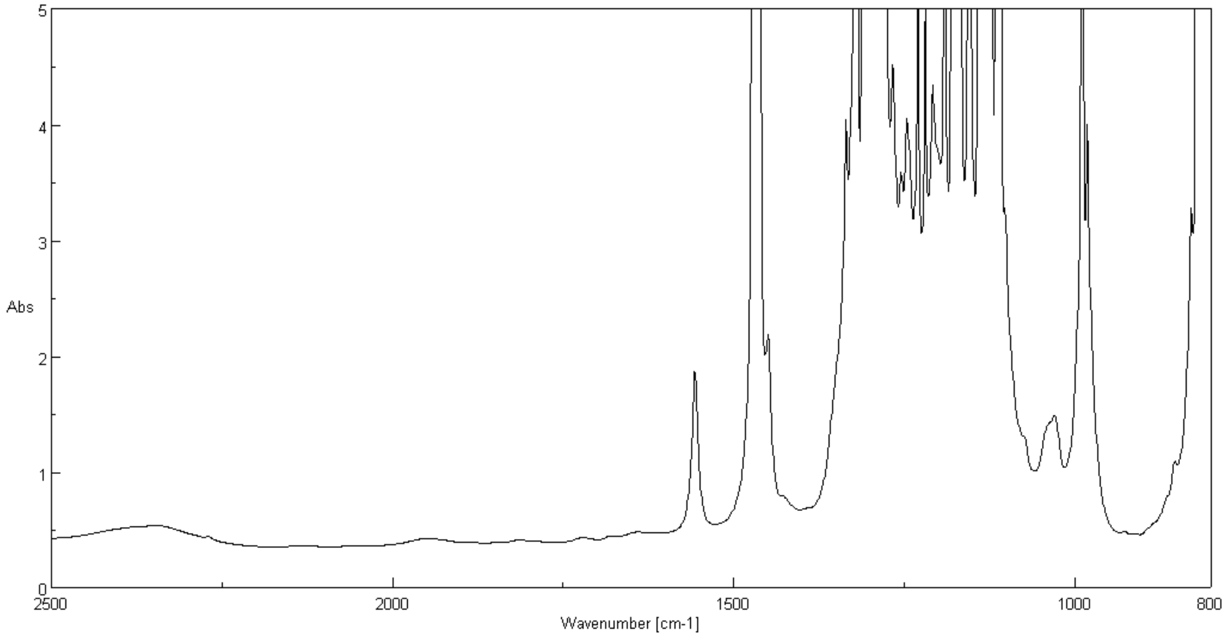

Figure 4.24. Transmission FTIR spectrum of UAXDHC1 grafted onto UAXDC1.

4.4 Conclusions and Future Work

By decreasing the TFE contents of these types of polymers below the level where crystallinity is observed, higher densities of acid sites are produced which should yield higher proton conductivities; however, the polymers lose the water insolubility required for operation in a fuel cell. Adding a curable ter-monomer into the polymer allows the chains to be crosslinked together to form a networked structure of effectively infinite molecular weight. Doing this regains water insolubility for the materials due to the entropy of dissolution involved with dissolving a material of such high molecular weight. This route allows water insoluble perfluorinated ionomers to be prepared with much lower EWs, allowing membranes with conductivities up to 5.5 times higher than commercial Nafion® 115 to be prepared. However, the downside to this route is the polymers have high swelling characteristics in water as they are only prevented from dissolving due to entropy, but without crystallinity no intermolecular forces exist to hold the polymer chains together and prevent swelling in water. To counteract this, the polymers can be impregnated in ePTFE to reduce the swelling characteristics somewhat while still retaining high proton conductivities.

The most promising area for future work in the author's opinion is the preparation of a wider array of grafted polymers. By producing a copolymer of TFE and 8CNVE with a molar ratio of monomers of around 5 : 1, a polymer with a high amount of crystallinity should be produced. A blend of this material and the copolymer of Dow and 8CNVE could then be cured through the triazine formation to produce a polymer with side chains that have more than 5-10 sulfonic acid sites each, instead of just 2 produced by the 3M Company. This should allow EWs to be lowered much more significantly than the 3M company could while retaining a polymer backbone with a high amount of crystallinity and low swelling characteristics. The new polymer produced would also likely have a very different structure and proton transport properties than Nafion® and other perfluorinated ionomers, perhaps showing unique and interesting conductivity profiles for use in PEMFCs.

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CHAPTER 5

PREPARATION OF ALTERNATING COPOLYMER OF VINYLIDENE DIFLUORIDE AND PSEPVE

5.1 Introduction

5.1.1 Introduction to VDF

Vinylidene difluoride (VDF) is a commonly used monomer, primarily for the preparation of poly(vinylidene difluoride) (PVDF). Industrial preparation of VDF is carried out by first adding hydrogen fluoride to acetylene to yield 1,1-difluoroethane (R152a). Selective chlorination of R152a to 1-chloro-1,1-difluoroethane (R142b) followed by a dehydrochlorination at elevated temperatures produces VDF. This partially fluorinated monomer shows benefits over other fluorinated monomers such as CTFE and TFE since it is non-toxic, does not explode, and can be easily purchased commercially.[1]

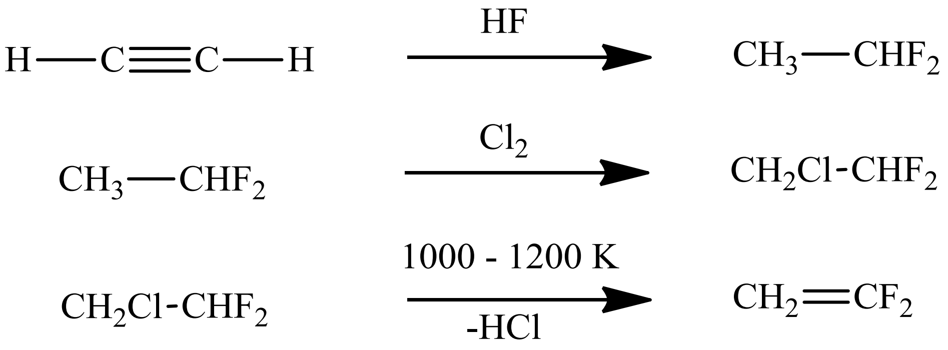

Figure 5.1. Industrial preparation of VDF

Homopolymerization of VDF to yield PVDF is typically carried out by emulsion or suspension polymerization similar to the preparation of PTFE, which will be discussed further in Chapter 6. Due to the monomer having both an electron rich and electron poor vinyl carbon, the homopolymerization favors a head-tail arrangement with 94-96.5% of the polymer having this orientation.[2] PVDF has found use in a wide array of markets such as a binder for the cathode and anode in lithium ion batteries, backing for photovoltaic cells, and as a paint additive on high value architectural structures to reduce the need for cleaning in difficult to reach places.[3]

While PVDF does contain CH_2 methylene groups in the backbone, the electronics of the polymer structure containing alternating CF_2 and CH_2 functional groups causes these CH_2 groups to become stable to radical, chain transfer effects under normal polymerization conditions. To prepare long chain branched polymers, materials that cannot be prepared for perfluorinated polymers, requires temperatures of 120 ˚C with a persulfate initiator.[4] By adding long chain branches, the physical properties and melt-flow characteristics of the polymer can be altered more easily than by simply changing molecular weight. However, PVDF is not stable in the presence of strong bases, thereby limiting the applications for which it can be used when compared to PTFE, FEP, and PFA materials.[2] Thus, while PVDF has a lower chemical stability than perfluorinated polymers, the structure and properties can be modified in ways not possible with perfluorinated materials, such as producing long chain branched polymers.

The VDF monomer is also used in many copolymers, specifically in the preparation of fluorinated elastomers. Common co-monomers with VDF include TFE, HFP, and CTFE in both random, graft, and block polymer configurations. One important aspect of these copolymers is that small amounts of the co-monomer can greatly alter the electronics and net dipole moments of the polymers. PVDF often adopts the alpha trans-gauche conformation where the proton and fluorine atoms from the γ-carbon atoms orient toward each other to maintain small amounts of hydrogen bonding, stabilizing the structure. Adding a co-monomer breaks this conformation, yielding materials with very different intra and intermolecular forces and giving new properties.[1]

5.1.2 Alternating Copolymers

Alternating copolymers can be prepared where the addition of the two monomers alternates throughout the polymer. While more difficult to prepare than random copolymers, polymers with this kind of orientation have interesting properties due to functional groups having a more regular environment and electronic structure. For two monomers to produce an alternating structure, the reactivity ratios (described in Chapter 2) should both be well below a value of 1.[5] While literature reactivity ratios are available for VDF and PSEPVE, their applicability to polymerizations under different conditions may be invalid, especially considering the high polymerization temperature of 134 ˚C under which the ratios were measured.[6]

More valid parameters are the Q and e values, which are measured independently of the comonomer and the conditions used. The Q value is based upon the reactivity of both the monomer and a propagating polymer chain with the monomer radical at the end. The e values are based upon the electronics of the monomer and whether electron donating or withdrawing groups are present. Reactivity ratios for the monomers can then be calculated using these Q and e values, which are found in the literature for many common monomers:[5]

$$r_a = \frac{Q_A}{Q_D} \cdot \exp\{-e_A(e_A - e_D)$$

$$r_d = \frac{Q_D}{Q_A} \cdot \exp\{-e_D(e_D - e_A)$$

It can be seen from these equations that to obtain reactivity ratios where the product trends toward a value of 0 (leading to an alternating copolymerization), the product of the exponents should also approach a value of 0. The product of these exponents gives $\exp\{-(e_A - e_D)^2]$, showing that to obtain reactivity ratios as low as possible, e_A and e_D the absolute value of the difference in e_D and e_A should be maximized.[5] This makes sense chemically as they suggest an electron rich and electron poor monomer pair will form an alternating copolymer, such as ethylene and tetrafluoroethylene, which are known to form an alternating polymer structure.

Two main theories of alternating copolymerization exist. The first is based upon a donor-acceptor complex being formed between the electron rich and electron poor monomer, causing this complex to be the actual reactive monomer. The second is based upon the activation energy being lower for the addition of the alternate monomer over homopolymerization. Each of these mechanisms has research that points toward its validity, suggesting a combination of the two mechanisms is more likely with the donor-acceptor complex being in equilibrium with the free monomers and the lowered activation energy playing a role in the alternating structure as well.[7]

5.1.3 Copolymers of VDF and PSEPVE

Both patents and journal articles are available on the copolymers of VDF and PSEPVE for fuel cell membranes.[6,8] While the patent does claim copolymers with PSEPVE contents between 0.5 and 50 mol%, no examples in the patent show the preparation of polymers anywhere near this high of PSEPVE content. In fact, the highest PSEPVE containing copolymer in the patent has a molar ratio of 1 PSEPVE : 10 VDF, appearing to be another case of the company increasing its patent position.[9] The polymer with the lowest VDF content prepared by Ameduri contains 77.7 mol% VDF and 22.3 mol% PSEPVE. Analysis of this polymer by ^{19}F NMR spectroscopy shows large peaks present around -90 ppm corresponding to CF_2 groups next to two CH_2 methylenes, or bulk VDF.[8a]

According to Ameduri *et. al.*, one of the main reasons for preparing the copolymers is the ability to use VDF as opposed to the more hazardous TFE.[8a] However, use of VDF in the copolymer has several drawbacks, primarily due to the fact that the CH_2 groups are not completely stable against radical attack and may decompose in the presence of peroxide radicals at the high temperatures inside a fuel cell and that hydrolysis cannot be performed with KOH since HF is eliminated from the backbone, decomposing the polymer. However, if new much improved polymers can be prepared with VDF as opposed to TFE, these limitations may prove worth overcoming.

Monomers that are known to form alternating copolymers with VDF include perfluoroisobutylene (PFIB), methyl trifluoroacerylate (MTFA) and α-(trifluoromethyl) acrylic acid (TFMAA). Of the three, only the e value of MTFA is known at 2.37 compared to 0.50 for VDF.[7] The e values for VDF and perfluorinated vinyl ether sulfonyl fluorides, such as PSEPVE, are 0.50 and 2.26, respectively.[7] The fact that the e values of PSEPVE and MTFA are so similar suggests that PSEPVE and VDF may form alternating copolymers as well. Additionally, the recorded reactivity ratios for PSEPVE and VDF under solution polymerization conditions are 0.07 and 0.54, respectively.[6] These values all suggest the possibility to prepare an alternating copolymer of VDF and PSEPVE, which is the lowest EW copolymer (with a molecular weight high enough to consider the material an actual polymer) that can be prepared with these kinds of monomers due to the inability of PSEPVE to truly homopolymerize.

A novel alternating copolymer of VDF and PSEPVE may offer some benefits in fuel cell applications as opposed to the more common copolymers of TFE and PSEPVE. A low EW alternating copolymer of VDF and PSEPVE would have the benefit of possessing a higher molecular weight than low EW copolymers of TFE and PSEPVE, which may be described more as oligomers than polymers. However, as the CH_2 group is less chemically stable and may have some downsides in fuel cell applications, direct fluorination of the material would allow the preparation of a perfluorinated material, allowing for the benefits from using VDF to prepare a high molecular weight, low EW polymer without the downside of the lower chemical stabilities. While direct fluorination is not as common industrially as the Simon's electrochemical fluorination (ECF), which uses an electrochemical process with a nickel anode in anhydrous hydrogen fluoride to form carbon fluorine bonds,[10] it can be employed more easily in an academic lab as it requires less setup than Simon's ECF.

5.2 Experimental

5.2.1 Bulk Polymerization UAXV1

Similar to previous bulk polymerizations with TFE, such as Example 2.2.10, to a 100-mL autoclave is added 115.75 g of degassed PSEPVE, and the autoclave is sealed and attached to the polymerization system before evacuating. The autoclave is then pressurized with 11 psig VDF and allowed to sit for 1 hour with a stirring rate of 200 RPM. Three 2.5 mL aliquots of a 0.083 M solution of pentafluoropropionyl peroxide (3P) in 2,3-dihydroperfluoropentane (HFC-4310) are added every 24 hours, and the VDF pressure is held at 11 psig throughout the course of the reaction. Workup is performed by venting the system, and the excess PSEPVE monomer is distilled out up to 160 ˚C and 80 mtorr, yielding 26.79 g of polymer.

NMR Spectra in R113: $\{CF_2^aCF^b[OCF_2^cCF^d(CF_3^e)OCF_2^fCF_2^gSO_2F^h]CH_2^yCF_2^z\}_n$:

^{19}F δa -122.3 (2F); δ^b -126.3 (1F, broad); δ^c -79.5 (4F); δ^d -144.6 (1F); δ^e -80.1 (3F); δ^f -79.2 (4F); δ^g -112.5 (2F); δ^h 42.3 (1F).

^{1}H δ^y 2.98 (broad, doublet)

Transmission FTIR Analysis (cm^{-1}): 3030 (w); 2990 (w); 1465 (s); 1397 (w); 1305 (s); 1245 (s); 1150 (s); 986 (s); 821, 797 (doublet, m).

5.2.2 Bulk Polymerization UAXV2

Similar to Example 5.2.1, to a 100-mL autoclave is added 119.50 g of degassed PSEPVE, and the autoclave is sealed and attached to the polymerization system before evacuating. The autoclave is then pressurized with 24 psig VDF. Three 2.6 mL aliquots of a 0.083 M solution of 3P in HFC-4310 are added every 24 hours before the system is vented, and the excess PSEPVE monomer is distilled out up to 160 ˚C and 80 mtorr, yielding 68.48 g of polymer. NMR and IR spectra are identical to UAXV1.

5.2.3 Bulk Polymerization UAXV3

Similar to Example 5.2.1, to a 100-mL autoclave is added 120 g of degassed PSEPVE and the autoclave is sealed and attached to the polymerization system before evacuating. The autoclave is then pressurized with 40 psig VDF. Three 2.6 mL aliquots of a 0.083 M solution of 3P in HFC-4310 are added every 24 hours before the system is vented, and the excess PSEPVE monomer is distilled out up to 160 ˚C and 80 mtorr, yielding more than 50 g of polymer. The resulting latex is extremely viscous and much polymer is lost in the workup making it impossible to know the exact yield. NMR and IR spectra are identical to UAXV1.

5.2.4 Bulk Polymerization UAXV4

Similar to Example 5.2.1, to a 100-mL autoclave is added 70 g of degassed PSEPVE, and the autoclave is sealed and attached to the polymerization system before evacuating. The autoclave is then pressurized with 95 psig VDF. Only two 1.55 mL aliquots of a 0.083 M solution of 3P in HFC-4310 are added every 24 hours before the stirring mechanism on the autoclave bogs down due to the polymerization having gone nearly to completion. The system is vented, and the excess PSEPVE monomer is distilled out up to 160 ˚C and 80 mtorr, yielding 77 g polymer.

5.2.5 Bulk Polymerization UAXV5

Similar to Example 5.2.1, to a 100-mL autoclave is added 85.05 g of degassed PSEPVE, and the autoclave is sealed and attached to the polymerization system before evacuating. The autoclave is then pressurized with 180 psig VDF. Two 2.6 mL aliquots of a 0.083 M solution of 3P in HFC-4310 are added every 24 hours before the system is vented, and the excess PSEPVE monomer is distilled out up to 160 ˚C and 80 mtorr, yielding 101.55 g of polymer.

5.2.6 Solution Polymerization UAXV6

To a 100-mL autoclave inside a dry box is added 58.83 g of HFC 4310 and 47.28 g of PSEPVE, both of which have been previously degassed by the freeze/pump/thaw method before sealing the autoclave and attaching it to the polymerization system. After evacuating the system and heating the autoclave to 35 ˚C, 80 psig of VDF is added to the autoclave with a stirring rate of 200 RPM. Using a Teledyne-Isco HPLC pump, 2.1 mL of a 0.083 M solution of 3P in HFC-4310 is added, and the reaction is allowed to proceed overnight with the VDF pressure maintained at 80 psig. Workup is performed by venting the unreacted VDF in a fume hood and distilling out excess monomer and solvent up to 160 ˚C and 80 mtorr, yielding 12.56 g of polymer. NMR spectra are similar to UAXV1 with a slightly increased intensity for the peaks around -90 ppm in the ^{19}F spectrum.

5.2.7 Bulk Polymerization UAXV7

To a 100-mL autoclave is added 85.11 g of degassed PSEPVE. and the autoclave is sealed and attached to the polymerization system before evacuating. The autoclave is then pressurized with 20 psig of VDF and evacuated again to remove all nitrogen before adding 36 psig VDF and heating to 35 ˚C. Using a Teledyne-Isco HPLC pump, 1.60 mL of a 0.134 M solution of 3P in HFC-4310 is added over 1 minute before changing the flow rate to

0.0027 mL/min for the next 5 hours 25 minutes. Workup is performed as before, yielding 24.05 g of polymer. NMR spectra of the product are similar to UAXV1.

5.2.8 Bulk Polymerization UAXR17

Using identical conditions as UAXV7 except with TFE as the co-monomer, to a 100 mL autoclave is added 85.01 g of degassed PSEPVE, and the autoclave is sealed and attached to the polymerization system before evacuating. The autoclave is then pressurized with 20 psig of neat TFE and evacuated again to remove all nitrogen before adding 35 psig TFE and heating to 35 ˚C. Using the HPLC pump, 1.60 mL of a 0.134 M solution of 3P in HFC-4310 is added over 1 minute before changing the flow rate to 0.0027 mL/min for the next 5 hours 27 minutes. Workup is performed as before, yielding 9.68 g of polymer.

NMR Spectra in R113: $\{CF_2^aCF^b[OCF_2^cCF^d(CF_3^e)OCF_2^fCF_2^gSO_2F^h]CF_2^yCF_2^z\}_n$:

^{19}F: δa -118.0; δ^b -138.8, -137.3 (depending on monomer arrangement); δ^c -78.8 (4F); δ^d -144.4 (1F); δ^e -80.1 (3F); δ^f -79.4 (4F); δ^g -112.7 (2F); δ^h 42.3 (1F); δ^y -120.8; δ^z -121.5.

^{1}H: No signal other than TMS.

ATR-FTIR Analysis (cm^{-1}): 1465 (s); 1304 (w); 1237 (s); 1188 (s); 1131 (s); 981 (s); 824, 795 (doublet, m).

5.2.9 Direct Fluorination of UAXV2 to UAXV2F

Inside an FEP reactor vessel with an outer diameter of 2.54 cm is placed a solution of 5.35 g of UAXV2 in 68.0 g of perfluorohexane. The FEP reactor vessel is placed inside a Rayonet photoreactor containing low-pressure mercury lamps that was inside a fume hood. With UV irradiation, a mixture of 20% F_2 in N_2 is slowly bubbled through this solution for 24 hours at room temperature followed by 16 hours at 50 ˚C. After removal of the perfluorohexane by distillation, 5.41 g of polymer remains that is shown to be completely fluorinated by infrared and ^{19}F NMR spectroscopies.

NMR Spectra in R113: $\{CF_2^aCF^b[OCF_2^cCF^d(CF_3^e)OCF_2^fCF_2^gSO_2F^h]CF_2^yCF_2^z\}_n$:

^{19}F: δa -118.0; δ^b -138.6 (1F, broad); δ^c -78.9 (4F); δ^d -144.4 (1F); δ^e -80.1 (3F); δ^f -79.3 (4F); δ^g -112.7 (2F); δ^h 42.3 (1F); δ^y -118.0; δ^z -120.0, -120.7.

^{1}H: No signal other than TMS.

ATR-FTIR Analysis (cm^{-1}): 1465 (s); 1305 (w); 1237 (s); 1198 (s); 1137 (s); 984 (s); 824, 795 (doublet, m).

5.2.10 Hydrolysis and Acidification of UAXV4

Hydrolysis is performed by twice using a 0.4 M ammonium carbonate solution in 1:1 H_2O/methanol overnight at 50 ˚C. The polymer is washed with water until the decanted water is neutral to litmus paper, at which point 15 M HNO_3 is added twice and allowed to sit for one hour. The polymer is again washed with DI water until the decanted water is neutral to litmus paper, and the polymer is dried at 160 ˚C and 10 mtorr for several hours.

ATR-FTIR Analysis (cm^{-1}): 2916 (w); 2847 (w); 1395 (w); 1231 (s); 1195 (s); 1135 (s); 1057 (s); 971 (s).

5.2.11 EW Titrations of UAXV4

A 100 mg sample of dry hydrolyzed and acidified UAXV4 is placed in 35 mL of 0.010 M trisodium phosphate overnight. A 25 mL aliquot of this solution is then titrated with a 0.010 M HNO_3 solution using a pH meter, recording the pH after every 1.0 mL of titrant is added. The HNO_3 is then standardized using a commercial 0.010 M NaOH solution. Determination of the EW is done by the following equations comparing the amount of offset in the x-axis (mL HNO_3

titrant) of the solution with polymer compared to the Na_3PO_4 standard, which for UAXV4 gives an EW of 600 - 700 g/mol between different samples:

$$mol\ SO_3H = (mL\ HNO_3\ titration\ graph\ of\ polymer\ is\ offset\ ) * (M\ HNO_3) * \left(\frac{35\ mL}{25\ mL}\right)$$

$$EW\ (\frac{g}{mol}) = \frac{grams\ UAXV4}{mol\ SO_3H}$$

5.2.12 Weight Percent Swelling Measurements

Measurement of the weight percent swelling of sample UAXV4 is performed by soaking a 2 mil thick piece of polymer in DI water for 1 hour at 20 ˚C. The membrane is then spot dried with a Kimwipe® until bulk dry, and the weight is recorded as 0.9313 g. After placing the membrane in a vacuum desiccator at 140 ˚C and 100 torr overnight the polymer is reweighed and the new weight of 0.3919 g polymer is recorded, giving a weight percent swelling of 140%.

5.2.13 Thermal Analysis of Samples

Differential scanning calorimetry (DSC) measurements are performed using approximately 10 mg of polymer sample in an aluminum pan. Using a TA Instruments Q200 instrument, the samples are quickly heated to 200 ˚C and allowed to anneal for two hours before cooling to -50 ˚C and reheating to 200 ˚C at a rate of 10 ˚C/min. Glass transition temperatures are reported as the midpoint of the thermal transition.

Thermal gravimetric analysis (TGA) is performed on a 15 mg sample in a platinum pan using a TA Instruments TGA 9250 under a nitrogen purge. Samples are typically heated to 120 ˚C and allowed to sit for one hour to remove any water seen from the atmosphere, before heating to a final temperature of 600 ˚C at a rate of 5.0 ˚C/min.

5.2.14 Melt Flow Analysis

The polymer resin is first cryoground into a powder using a Spex Sample Prep Freeze Mill 6870. Ten grams of UAXV4 resin is placed into the instrument and chilled in liquid nitrogen before staring the cryogrinding process with settings of 12 cycles, 3 minute precool, 5 minute runtime, 4 minute cool time, and 14 cycles per second. After warming to room temperature, a powder of the polymer is obtained.

Melt flow analysis is then performed using a Testing Machines Inc. melt flow indexer XNR-400. After heating the instrument to the desired operating temperature, the resin powder is added and allowed to heat for 2 minutes before adding a 1200 g weight. The machine is then started and three polymer samples are cutoff every minute where the average mass of the three samples is taken as the melt flow in g/min.

5.3 Results and Discussion

5.3.1 Bulk Polymerizations UAXV1 - UAXV5

While copolymers of VDF and PSEPVE have some drawbacks, such as lower chemical resistances and a more difficult hydrolysis step, it was hypothesized that high molecular weight, low EW copolymers could be prepared more easily with VDF than TFE. The literature reactivity ratios of TFE and PSEPVE of 9.0 and 0.04, respectively, show that both monomers prefer the subsequent addition of TFE in the propagation reaction.[11] Thus, the only way to obtain low EW materials with TFE is to lower the TFE pressures, which has the drawback of producing low molecular weight materials since the rate constants towards addition of PSEPVE are so low.

However, the literature reactivity ratio for VDF and PSEPVE of 0.57 and 0.07, respectively, show it should be possible to produce high molecular weight, low EW samples.[6] These reactivity ratios show that for a VDF terminated, propagating chain the rate of addition for a PSEPVE monomer is twice as high as for another VDF monomer. Thus, higher VDF pressures can be used while still producing a low EW material, allowing for higher molecular weight materials to be produced. The e value for PSEPVE, 2.26, being close to MTFA, 2.37, suggests it is possible to form an alternating copolymer structure. Under high VDF concentrations it is known in the literature that materials with three or more VDF monomers per PSEPVE can be produced. Thus, increasing the concentration of PSEPVE, which does not readily homopolymerize, and by using bulk polymerization conditions and lower VDF pressures increases the likelihood of producing the desired alternating copolymer.

VDF pressures are controlled by a two-stage regulator on the cylinder to keep a constant pressure of VDF throughout the polymerization without requiring an operator monitoring the polymerization. Using the current polymerization system and the preparative method for TFE (both described in Chapter 1), this two-stage regulator gives VDF a distinct advantage over TFE. The exothermic removal of CO_2 *in situ* with Ascarite® makes use of a two-stage regulator with TFE dangerous. Without a human operator to control the rate that the TFE and CO_2 is added to the Ascarite® scrubber, the rate of addition may be too high and lead to unsafe temperatures and perhaps deflagration. Using the two-stage regulator with VDF is not a concern as VDF is not explosive and the monomer is already pure and does not require the Ascarite® scrubber.

To obtain a maximum concentration of PSEPVE monomer, the conditions of a bulk polymerization are employed. Similar to the homopolymerization of PSEPVE, detailed in Chapter 3, aliquots of 3P initiator are added every 24 hours to the polymerizations running at room temperature (20 ˚C). At 25 ˚C, 3P has a half-life of 16 hours, suggesting the half-life for these reactions at 20 ˚C is around 24 hours. By adding aliquots of initiator every 24 hours, one attempts to obtain a steady-state radical flux. Three initiator additions are performed for samples

UAXV1, UAXV2, and UAXV3, while polymerizations UAXV4 and UAXV5 have only two additions, as these polymerizations have already gone nearly to completion after the second addition. Based upon the high conversions of monomer to polymer (see Table 5.1), multiple additions of initiator are not required, and likely cause high degrees of chain transfer between growing polymer chains and the CH_2 groups in polymers already produced. However, the conditions are kept constant here with multiple initiator additions to compare the materials produced with different pressures of VDF.

Table 5.1 - UAXV Bulk Copolymerizations

Sample	PSEPVE (g)	VDF (psig)	Total Initiator (mmol)	Polymer (g)
UAXV1	115.75	11	0.623	26.77
UAXV2	119.50	24	0.647	68.48
UAXV3	120.	40	0.647	>50
UAXV4	70.	95	0.257	76.56
UAXV5	85.05	180	0.295	101.55

Workup is performed similarly to the copolymerizations of TFE and PSEPVE from Chapter 2 where the resin is heated to 150 ˚C at 100 torr overnight to remove all remaining monomer from the sample, which can be confirmed by ^{19}F NMR spectroscopy of the polymers dissolved in R113.

5.3.2 Analysis of VDF and PSEPVE Copolymers

Samples UAXV1, UAXV2, and UAXV3 are soluble in refluxing R113, allowing NMR characterization to be performed on the unhydrolyzed polymer (see Figures 5.2 and 5.3). Of note are the barely detectable peaks around -90 ppm in Figure 5.2 that correspond to bulk VDF. The absence of bulk VDF and inability of PSEPVE to readily homopolymerize confirm a molar ratio of nearly 1 VDF : 1 PSEPVE. Proving the desired alternating structure are the peaks at -127.2 ppm, corresponding to the CF from the backbone, and the cluster of peaks from -111.5 to -112.5 ppm, corresponding to the CF_2 from VDF. The peak seen at -127.2 ppm shifts downfield

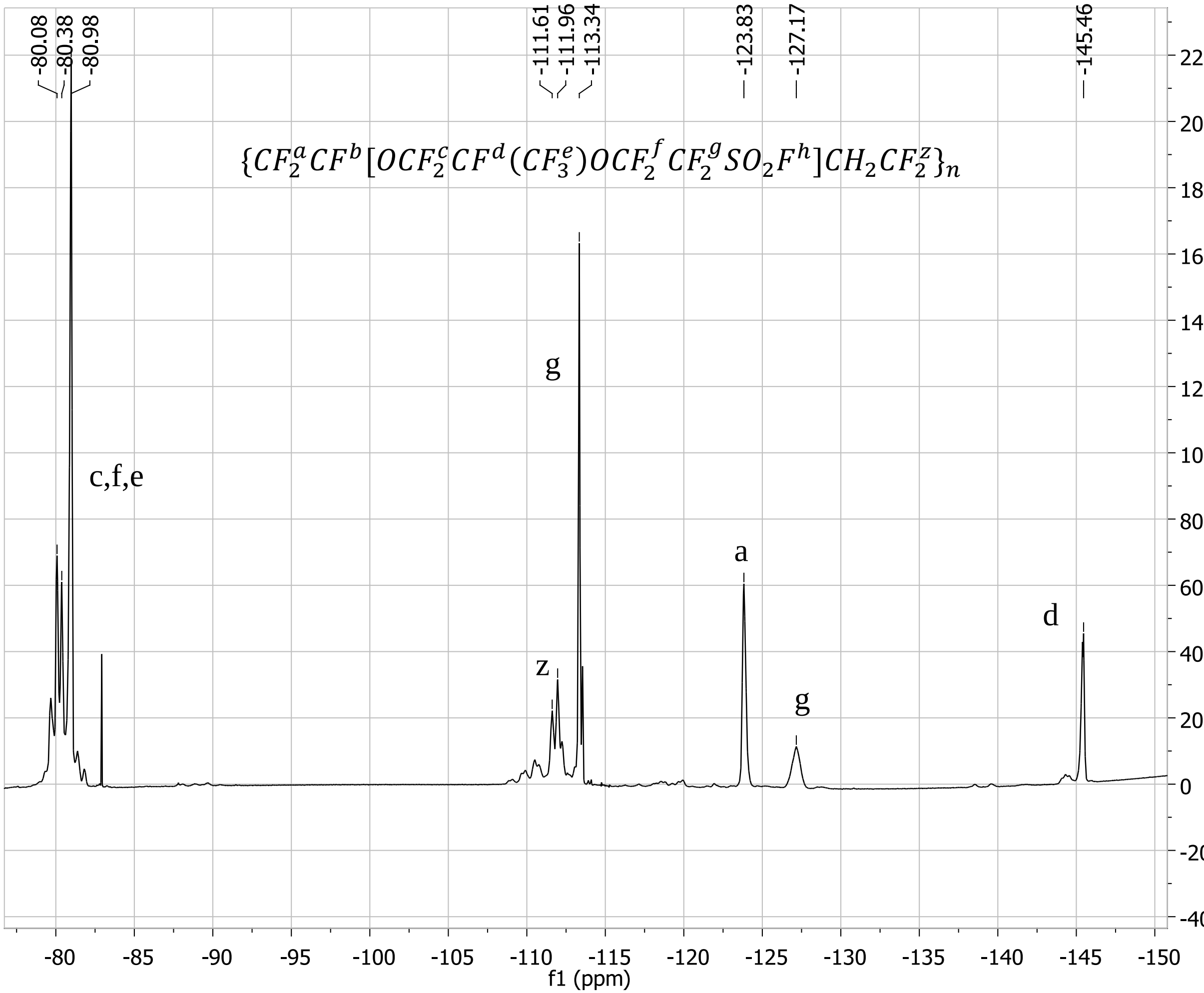

Figure 5.2. ^{19}F NMR spectrum of UAXV3 dissolved in R113. Identical to UAXV1 and UAXV2.

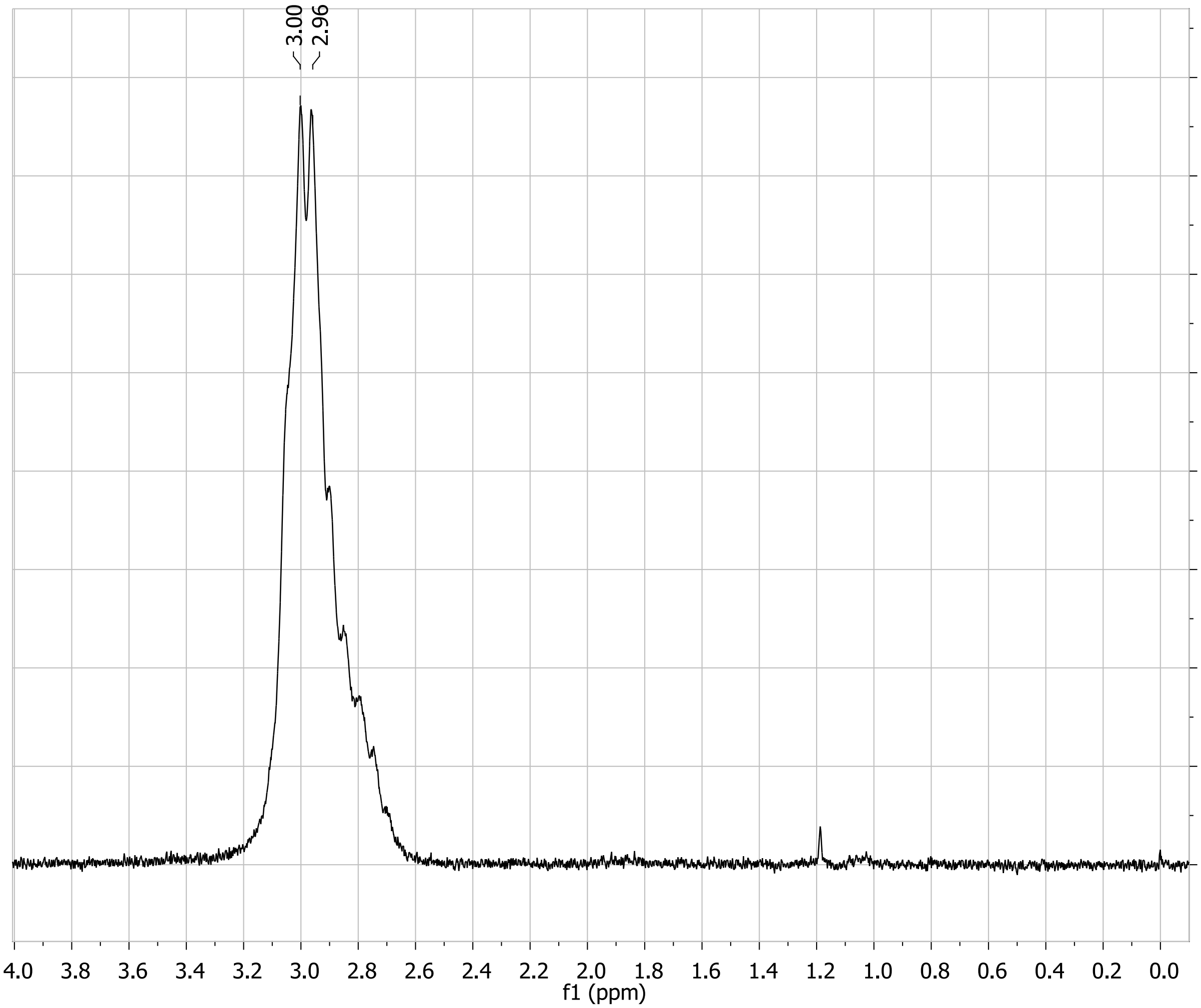

Figure 5.3. ^{1}H NMR Spectrum of UAXV3 in R113. Representative of UAXV1 and UAXV2.

from -138.9 ppm, where it is seen in TFE copolymers, due to the fact that this group is next to a single CH_2 methylene. The peaks around -112 ppm are shifted upfield from their usual chemical shift in bulk VDF, -90 ppm, due to being bonded to a CF_2 and CH_2 instead of two CH_2 groups as in bulk VDF. Two small peaks are seen at -139.6 and -138.6 ppm, corresponding to the CF in the backbone next to two CF_2 groups, which occurs from the reverse addition of VDF and bulk PSEPVE segments, respectively. Figure 5.3 shows the presence of the CH_2 functional groups, but the broadness prevents any true interpretation about the peaks other than their presence. While a few impurities exist such as small amounts of bulk VDF segments and the reverse addition product of VDF, as seen in PVDF, overall the NMR spectra confirm the desired alternating copolymer for all three samples prepared with VDF pressures of 11, 24, and 40 psig.

Samples UAXV4 and UAXV5 are not soluble in common fluorinated solvents such as R113 or perfluorohexane when heated up to 150 ˚C in a stainless steel cylinder for three days. While swelling occurs, no detectable amount of polymer is dissolved in the solvents as verified by ^{19}F NMR spectroscopy. Additionally, as PVDF homopolymer is soluble in acetone, it has been attempted to dissolve these copolymers in acetone by heating up to 150 ˚C under pressure for three days without success. However, UAXV4 is mostly soluble in perfluoro(perhydrophenanthrene) after heating to 280 ˚C for three days. While the solvent is only 80%, pure and the ^{19}F NMR spectrum of the solvent covers the spectrum from -110 to -150 ppm, making it difficult to obtain a signal from the polymer, the S-F and CF_3 peaks are detectable in the ^{19}F NMR spectrum. As shown in Figure 5.4, the -90 ppm region contains no solvent peaks and only very small peaks are present from bulk VDF in the polymer when compared to the intensity of the peaks at -81.1, -81.5, and -82.1 ppm, confirming a nearly alternating structure for the fraction of UAXV4 dissolved in perfluoro(perhydrophenanthrene).

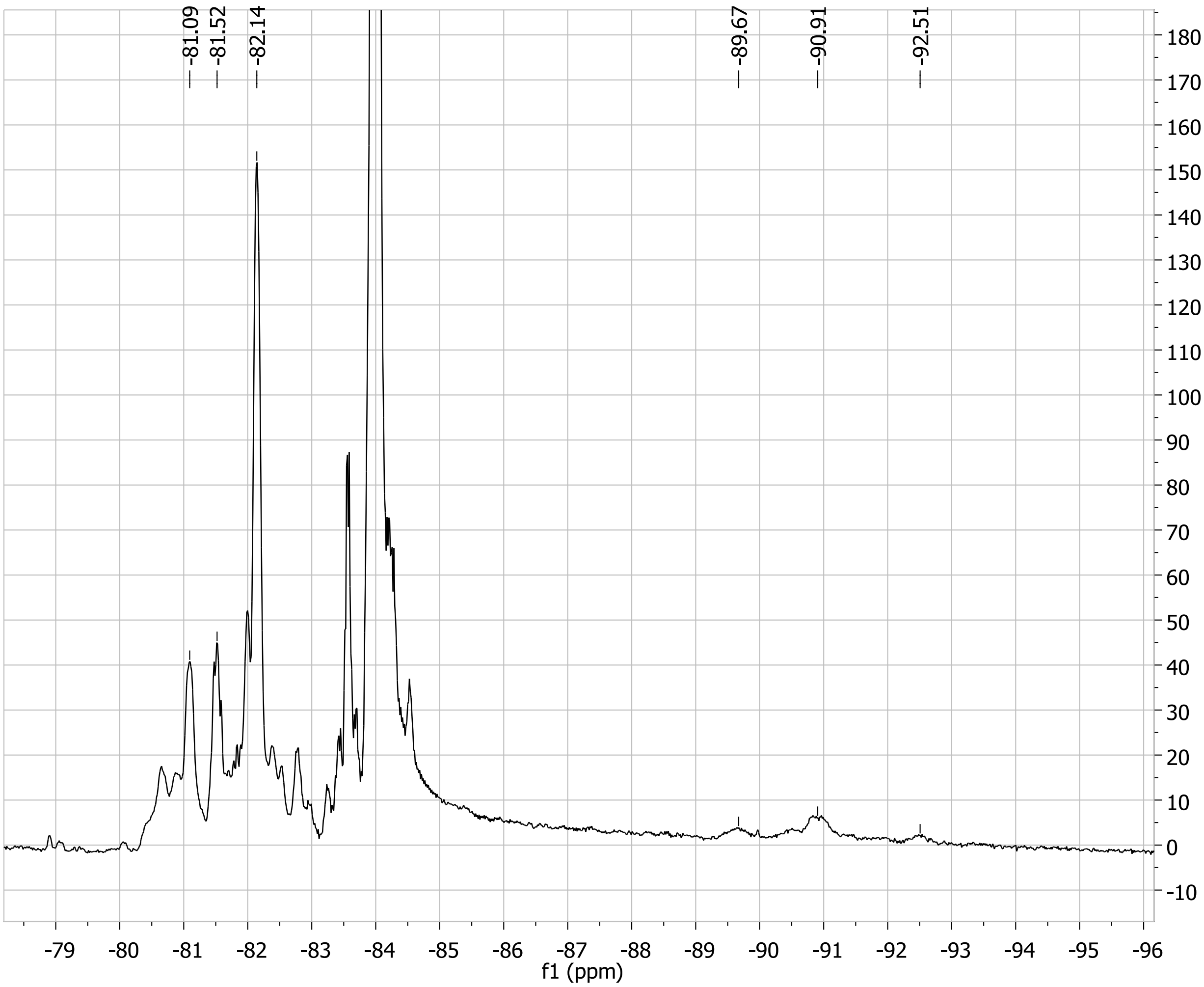

Figure 5.4. ^{19}F NMR spectrum of UAXV4 dissolved in perfluoro(perhydrophenanthrene)

Only one TGA measurement, presented in Figure 5.5, was performed on sample UAXV2, showing a 5% T_d of 391 ˚C, a much higher thermal stability than low EW TFE copolymers, such as UAXR16 seen in Figure 2.20, likely due to the higher molecular weights. Glass transition temperatures between samples UAXV2 to UAXV5 decrease from -17.94 ˚C to -18.36 ˚C to -20.36 ˚C to -20.78 ˚C, respectively. These small decreases in the glass transition temperatures suggest no significant difference in the polymer structure between samples. The polymers remain translucent suggesting a low degree of crystallinity. No crystalline transitions and/or melting points are seen in the DSC for any of these polymer samples heated up to 300 ˚C, again suggesting almost no crystallinity is present in the materials, as expected with such a high content of PSEPVE with the bulky side chain.

Melt flow analysis on the samples is performed in an attempt to obtain relative molecular weight data. Sample UAXV3, prepared with 40 psig VDF, has a melt flow too high to measure under the same conditions used for commercial Nafion® 1100, 270 ˚C with a 1200 g load, which gives a melt flow of 0.5 - 1.5 g/min under these conditions. This fact suggests low crystallinity and low molecular weight since high molecular weight polymer samples tend to have high amounts of chain entanglement and lower melt flow properties. Samples UAXV4 and UAXV5 have almost no melt flow with a 1200 g load at 340 ˚C, the point that the polymer begins to decompose in air. The absence of a crystalline melting point up to 340 ˚C by DSC and low melt flow characteristic suggests these samples prepared with high VDF pressures have no crystallinity and are either highly branched or crosslinked.

Hydrolysis of the samples is performed with ammonium carbonate.[8b] Stronger bases such as alkali metal hydroxides begin removing protons from the backbone and decomposing the polymer, which becomes visually dark black. Use of ammonium carbonate hydrolyzes the

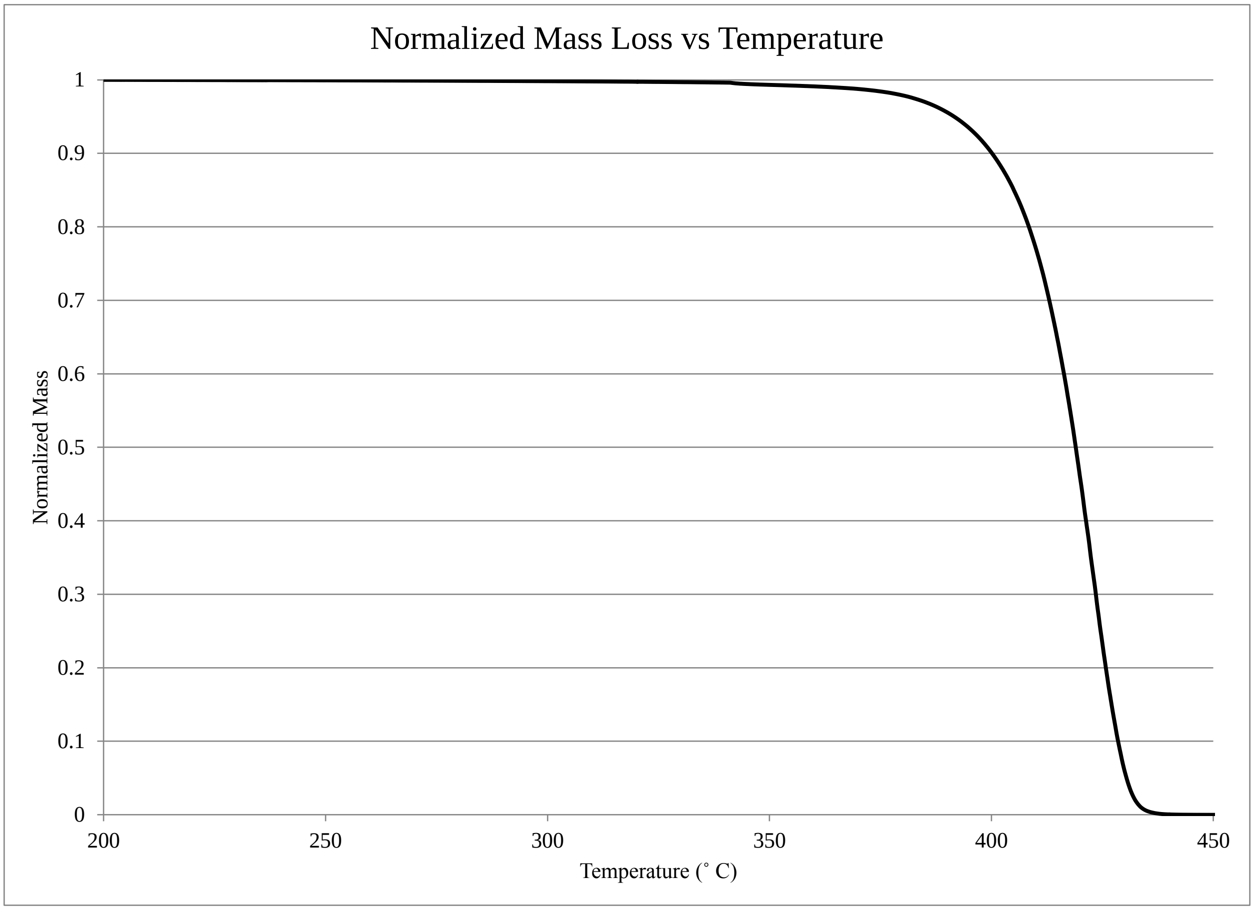

Figure 5.5. Plot of UAXV2 TGA data.

polymer, according to infrared spectroscopy by the disappearance of the peak attributed to the SO_2F functional group at 1457 cm^{-1} seen in Figure 5.6 and appearance of the peak attributed to the sulfonate at 1056 cm^{-1} seen in Figure 5.7, while only turning the polymer slightly yellow in color. Acidification of the sample is done by twice placing it in 80 ˚C 15M HNO_3 for 30 minutes, as done previously with the TFE co- and terpolymers. After hydrolysis and acidification, sample UAXV4 remains insoluble in boiling water for 24 hours.

Equivalent weight titrations of the acidified polymer involve a back titration of excess 0.01 M trisodium phosphate with 0.01 M nitric acid. Titration of the excess trisodium phosphate solution after overnight with 100 mg of polymer is compared to the titration of the 0.01 M trisodium phosphate standard. The amount of acid groups present in the polymer can be determined by comparing the two titrations and determining how much base is neutralized overnight with the acidified polymer. Titrations of UAXV4 show a large error bar with EWs between 600 - 700 g/mol. These EWs suggest molar VDF : PSEPVE ratios of 2.5-4 : 1, well above that predicted by NMR spectroscopy and mass balance of monomer used to polymer obtained suggests possible. This discrepancy seems to suggest some decomposition of the polymer and loss of acid groups during hydrolysis. The likely mechanism for this is hydrogen abstraction from the CH_2 group in the backbone to form a carbanion, which then rearranges to form a vinyl group in the backbone with elimination of the PSEPVE side chain.

Weight percent swelling of hydrolyzed and acidified UAXV4 is measured to be 140%. While some decomposition occurs during hydrolysis such that the EW is not as low as the hypothetical 510 g/mol, this degree of swelling is remarkably low for such a low EW sample. Absence of a crystalline melting point in the samples by DSC analysis indicates that little or no crystallinity exists in the samples, and thus the low swelling cannot be due to crystallinity as seen

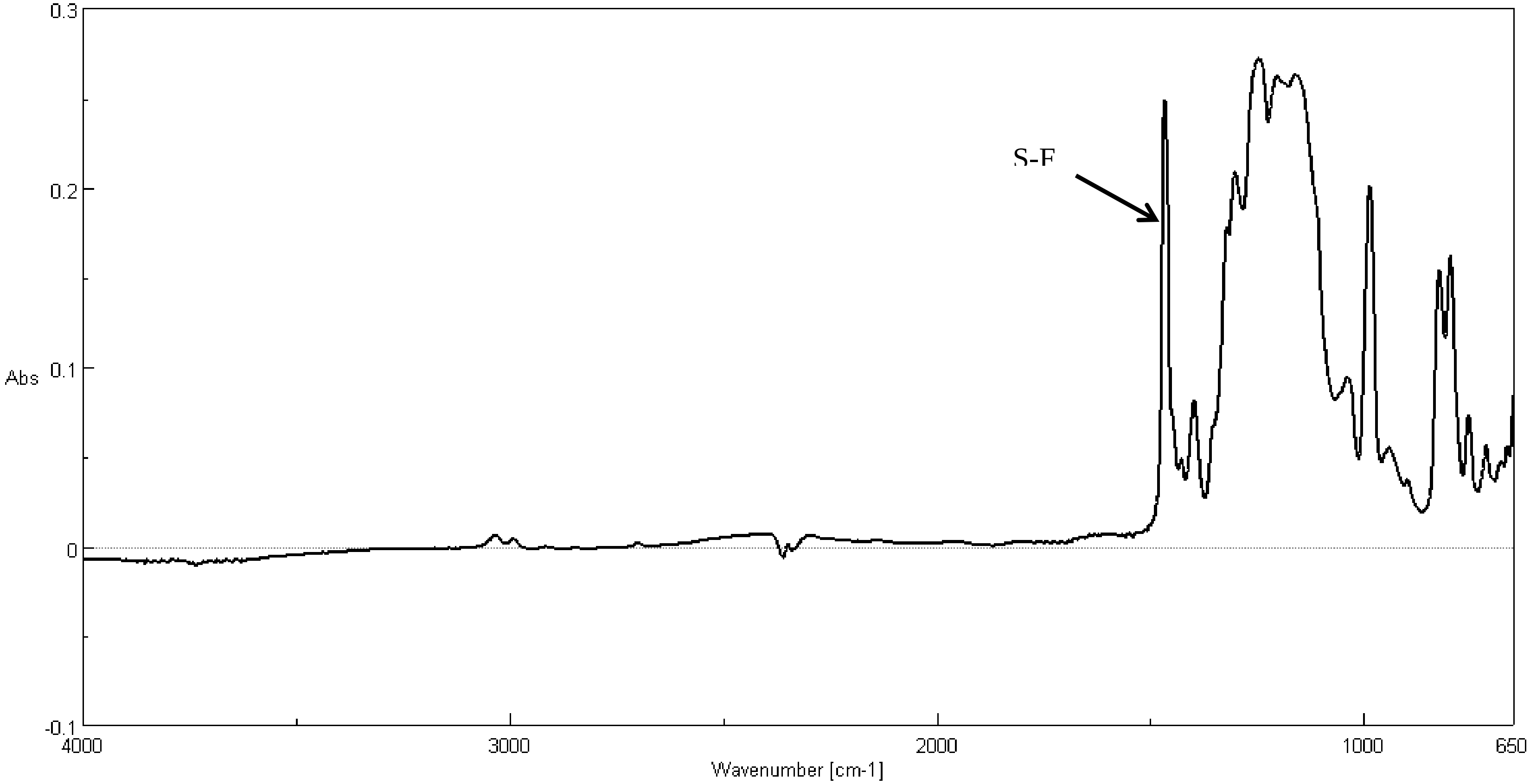

Figure 5.6. ATR-FTIR spectrum of UAXV2.

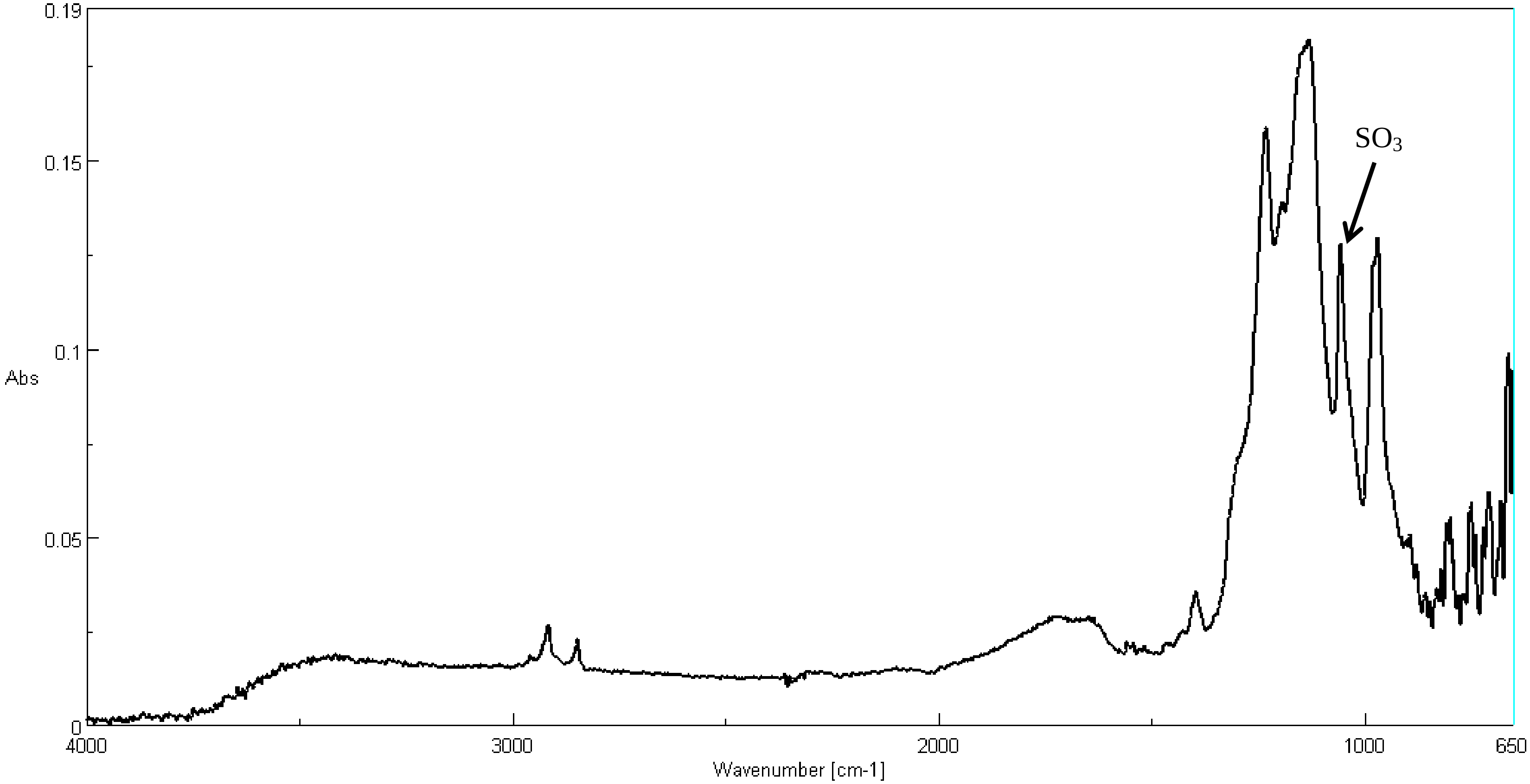

Figure 5.7. ATR-FTIR spectrum of hydrolyzed and acidifed UAXV4.

in higher EW samples. The low swelling may be due to better packing due to the more regular alternating structure, as is seen with ETFE where chains pack in the x-y direction while every four carbons has a hydrogen oriented into the z-direction, which here could be the side chain.[12] Alternatively, the low swelling may be due to the decomposition during hydrolysis removing some side chains and adding crystallinity back into the polymer with large segments of the polymer having no side chain to break up the crystallinity.

5.3.3 Solution Copolymerization of VDF and PSEPVE

To determine the viability of preparing an alternating copolymer with solution techniques instead of a bulk polymerization, sample UAXV6 is prepared. With a lower concentration of PSEPVE due to having perfluorohexane as a solvent, it is hypothesized that a material with a greater VDF content should be produced. Analysis of the polymer dissolved in R113 by ^{19}F NMR spectroscopy (see Figure 5.8) does indeed show a greater intensity of peaks in the -90 to -95 ppm range; however, the material still appears to mostly be a 1 to 1, alternating copolymer as the peaks are still not intense.

The most telling peak in the spectrum occurs for the CF methine fluorine in the backbone of the polymer. In samples UAXV1, UAXV2, and UAXV3 a single peak occurs at -126.3 ppm in the ^{19}F NMR spectrum. For sample UAXV6 this peak exists along with another smaller peak at -127.9 ppm. This smaller peak occurs for CF groups in the backbone where two VDF monomers add sequentially, $[C\mathbf{F}(OR_f)CH_2CF_2CH_2CF_2]$, not the desired alternating structure. An integral ratio of 4 : 1 for these two peaks shows roughly 20% bulk VDF in sample UAXV6. Thus, by using a solution polymerization it becomes less likely to form a truly alternating structure despite still preparing low EW materials. Unfortunately, the literature solution copolymerizations of VDF and PSEPVE give no experimental conditions on the concentrations

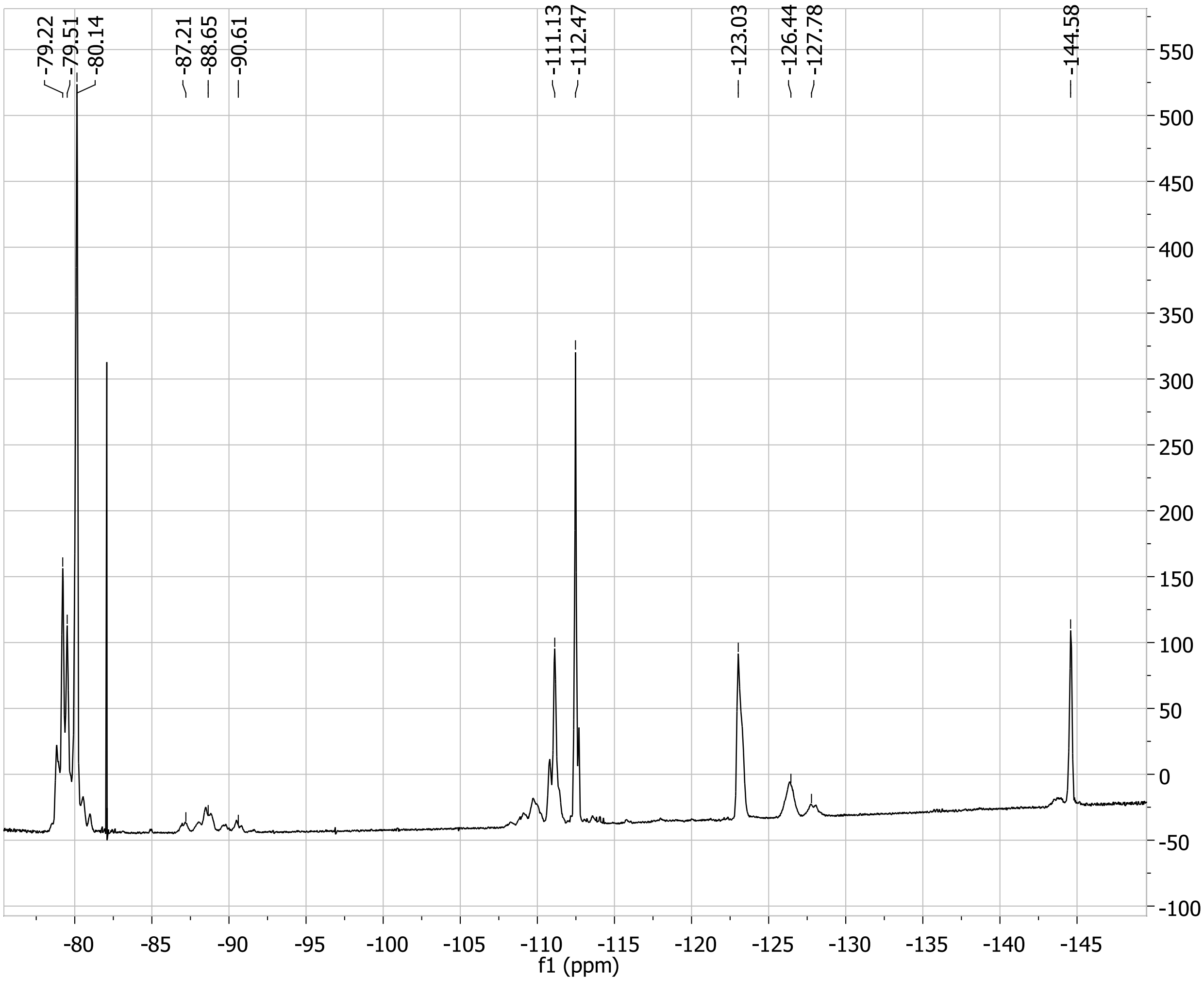

Figure 5.8. ^{19}F NMR spectrum of UAXV6 solution copolymer in R113

of PSEPVE or pressures of VDF, making it impossible to compare the conditions and know what conditions are required for preparation of these high EW materials in the literature.[6] No further time was spent attempting to recreate high EW, VDF copolymers already seen in the literature.

5.3.4 Bulk Polymerizations UAXV7 and UAXR17

Two more bulk polymerizations UAXV7 and UAXR17 are performed under more ideal conditions with a 5-hour reaction time and without going to such a high conversion of monomers. The only difference in these two polymerizations is the co-monomer, VDF (UAXV7) or TFE (UAXR17). Polymerization UAXV7 produces 24.05 g of product, while UAXR17 produces only 9.68 g, suggesting a higher molecular weight for the low EW copolymer of VDF and PSEPVE versus the low EW copolymer of TFE and PSEPVE. This yield discrepancy is even more pronounced when one takes into account the molar mass of VDF (62 g/mol) compared to TFE (100 g/mol), indicating that much longer chains are produced with VDF than TFE.

Analysis of UAXV7 in R113 by ^{19}F NMR spectroscopy confirms the alternating structure described previously with a spectrum similar to that shown in Figure 5.1. However, ^{19}F NMR spectral analysis of UAXR17 shows that even with a low EW, an alternating structure is not formed with TFE, as shown in Figure 5.9. Similar to UAXV6, the solution copolymerization of VDF and PSEPVE in C_6F_{14}, two peaks are seen for the CF region for the backbone of sample UAXR17. The larger peak at -138.8 ppm corresponds to the CF in the backbone when a PSEPVE and TFE monomer react sequentially. The smaller peak at -137.3 ppm occurs for the CF in the backbone when two PSEPVE monomers react sequentially. Even with the low EW, around 550 g/mol for UAXR17, and the very low reactivity ratio of

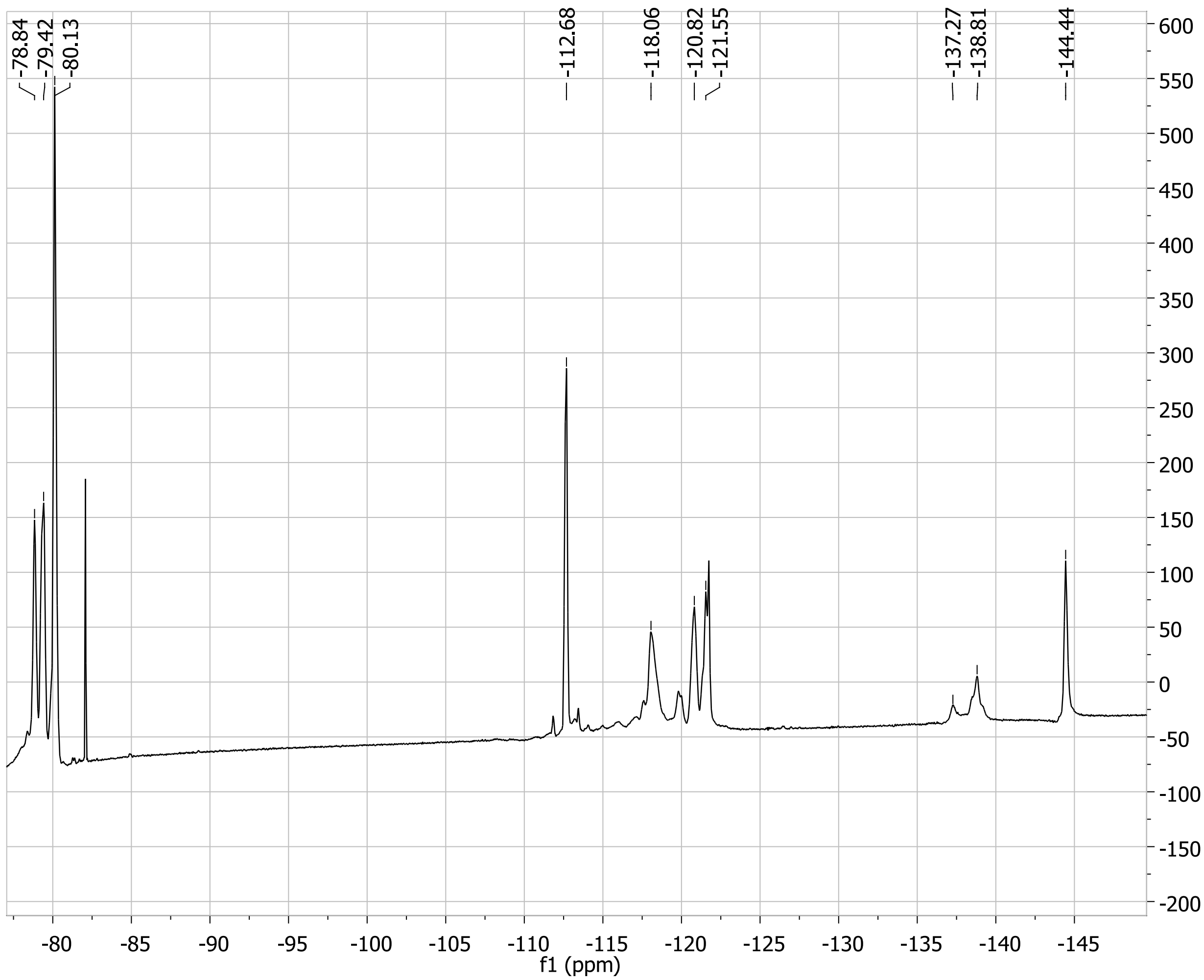

Figure 5.9. ^{19}F NMR spectrum of UAXR17 dissolved in R113.

PSEPVE with TFE, 0.04, segments of bulk PSEPVE still exist in the polymer. Therefore, the use of VDF as opposed to TFE greatly increases the ability to produce lower EW materials with high molecular weights.

Polymerizations UAXV1-5 are performed with similar conditions to the homopolymers, a two to three day reaction time, in an attempt to increase the amount of polymer produced. Sample UAXV7 shows that it is possible to use a shorter reaction time, which would give more of a chance to develop a commercially viable scaled-up procedure while still obtaining acceptable yields of polymer. When using VDF to prepare copolymers with PSEPVE, the electronics of the monomers actually favor producing lower EW samples, allowing higher molecular weights and yields of product to be obtained. Thus, the extreme conditions of long reaction times and removing all chain transfer agents are not as necessary to produce low EW materials.

5.3.5 Direct Fluorination of UAXV2

As PVDF is stable to elemental fluorine under most conditions,[2] it is not too surprising that UAXV2 is stable to 20% elemental fluorine in nitrogen for 3 days at room temperature. Addition of UV irradiation using a Rayonet reactor with low pressure mercury lamps allows the direct fluorination of UAXV2 to a perfluorinated material. With an absorbance in the UV-vis spectrum at 315 nm and fluorine-fluorine bond energy of 37 kcal/mol, elemental fluorine has the most readily cleavable bond in the reaction medium. The reactive species in a direct fluorination are fluorine radicals, which initiate a catalytic reaction yielding a new carbon-fluorine bond and regenerating the fluorine radical, as shown in Figure 5.10. Since the hydrogen content in these polymers is so low, recombination of fluorine radicals to form elemental fluorine likely happens with a high rate compared to the rate of fluorination of the backbone. Thus, increasing the rate of generation of fluorine radicals by the addition of UV irradiation greatly increases the rate of fluorination of the polymer.

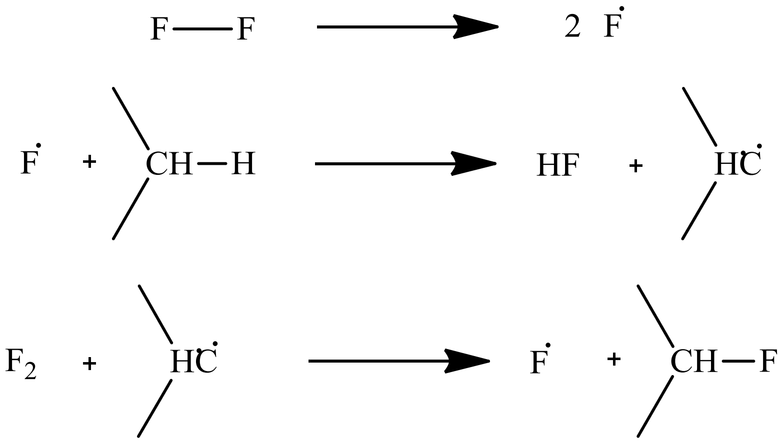

Figure 5.10. Direct fluorination reaction mechanism.

Analysis of the resulting polymer is performed by IR and multi-nuclear NMR spectroscopies. As shown in Figure 5.11, after fluorination the C-H stretches at 2917 and 2848 cm^{-1} and the CH_2 bend at 1398 cm^{-1} have both disappeared, and the resulting spectrum matches well with that of a low EW TFE copolymer. The ^{19}F NMR spectrum of the polymer dissolved in R113 (see Figure 5.12) shows that the CF_2 group from VDF previously around -111 ppm has shifted upfield to -119 to -123 ppm after fluorination, while the CF group from the backbone has shifted upfield from -126.4 ppm to -138.4 ppm. Both of these shifts are due to the fluorination of the CH_2 functional group to CF_2 group, and the resulting ^{19}F NMR spectrum appears similar to that of the low EW TFE copolymer UAXR17, with slight impurities from perfluorohexane seen at -84.7, -124.3, and -126.9 ppm. Additionally, the broad peak centered at 3.0 ppm in the ^{1}H NMR spectrum disappears completely upon fluorination, suggesting complete conversion to a perfluorinated material, as seen when comparing Figure 5.13 to Figure 5.3.

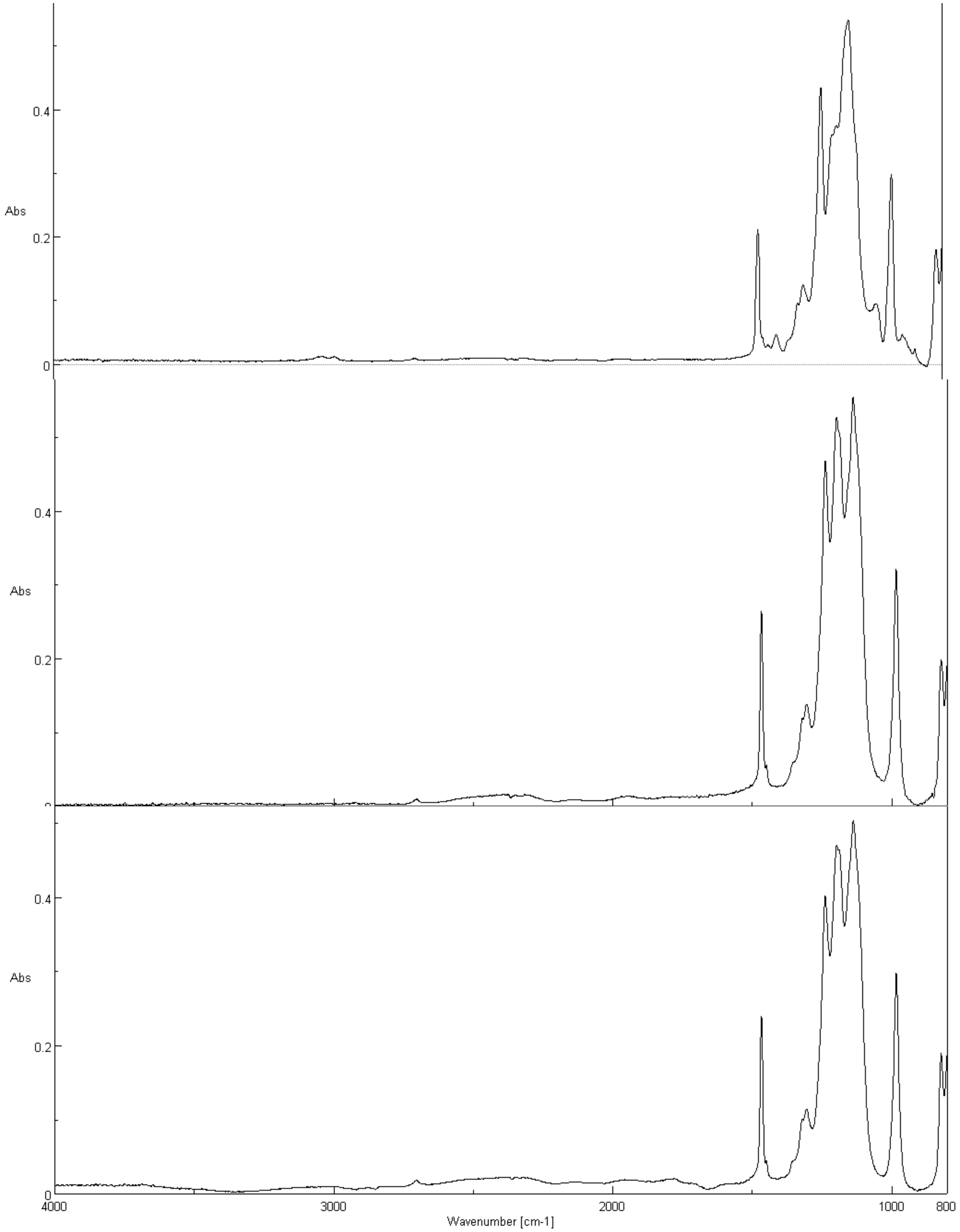

Figure 5.11. FTIR spectra of (top) UAXV2; (middle) UAXV2 after direct fluorination; (bottom) UAXR17 (550 EW copolymer of TFE and PSEPVE).

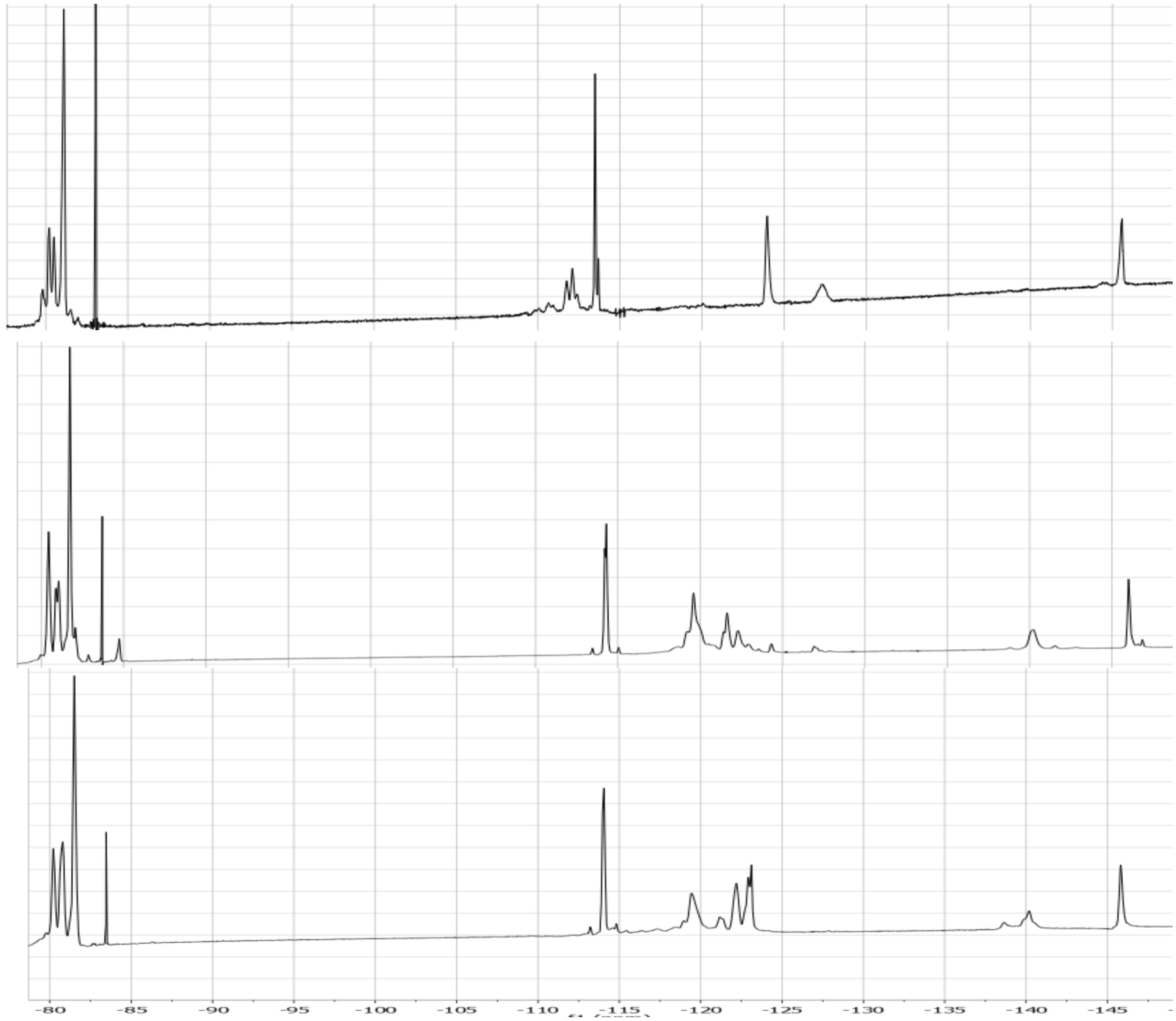

Figure 5.12. ^{19}F NMR spectra of sulfonyl fluoride samples dissolved in R113: (top) UAXV2; (middle) UAXV2 after direct fluorination; (bottom) UAXR17 (550 EW copolymer of TFE and PSEPVE).

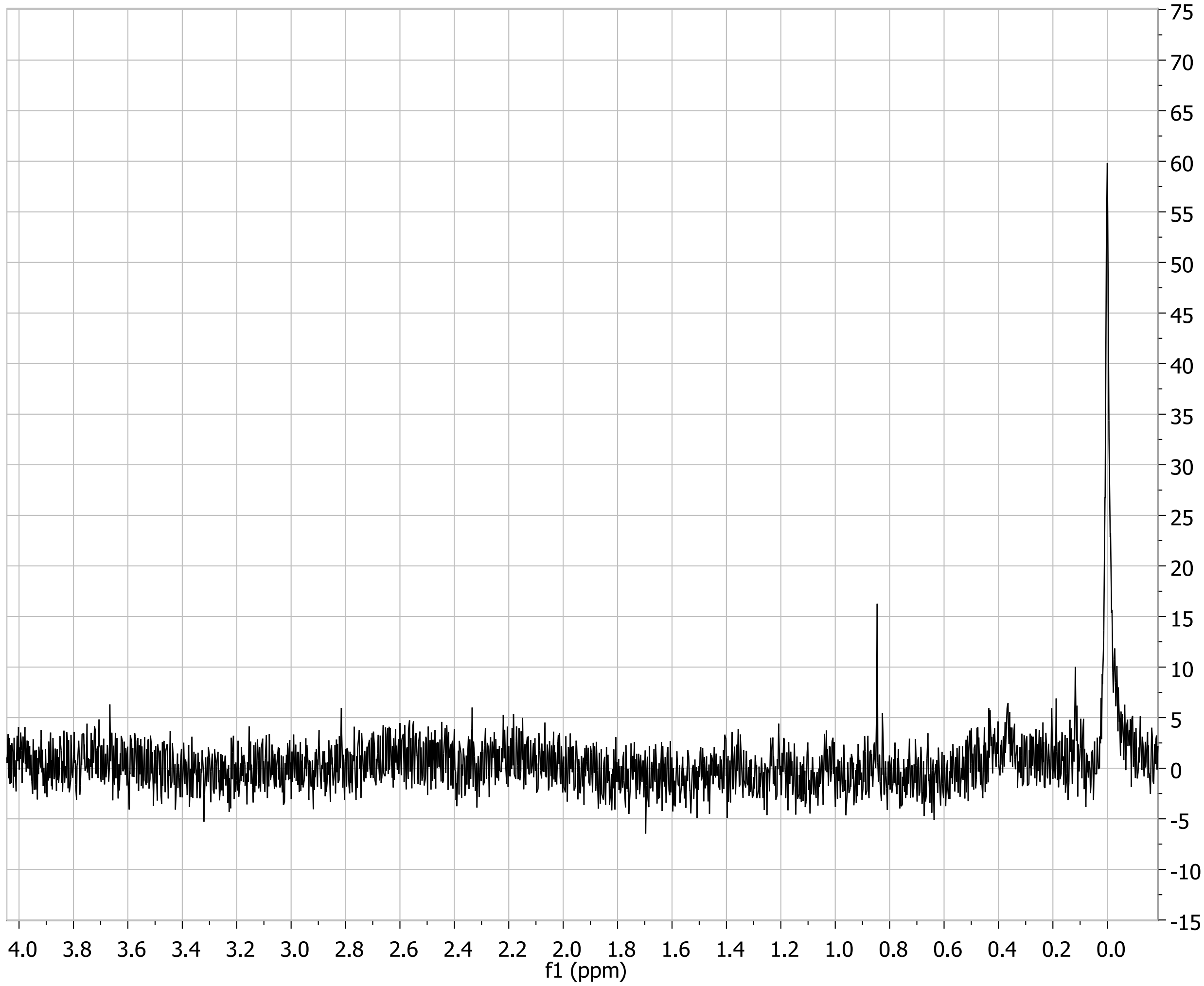

Figure 5.13. ^{1}H NMR spectrum of UAXV2 after direct fluorination dissolved in R113.

5.3.6 Future Work

Future work in this area would be to perform more bulk copolymerizations of PSEPVE with VDF under an increased variety of conditions. The most interesting polymerization condition would be preparing polymers under high pressures of VDF without going to such high conversions of monomer (that likely leads to chain transfer and branching or crosslinking of polymer chains). If the resulting higher molecular weight, alternating polymer structure prepared without branching or crosslinking is soluble in fluorinated solvents, better characterization could be performed with ^{19}F NMR spectroscopy. However, if the material remains insoluble in fluorinated solvents, solid state NMR on these materials should give a better idea of the structure of the polymer.

One downside to direct fluorination reaction mechanism is UV light likely causes some C-C bond cleavage, either removing some side chains or lowering molecular weight. Another possible fluorination route would involve the use of a sealed system with fluorine at higher temperatures and pressures to drive the reaction. By not using UV irradiation the amount of decomposition of the polymer could be lower. Additionally, the sealed system would allow direct fluorination of the higher molecular weight samples that are insoluble in perfluorohexane. Either thin membranes could be prepared to allow fluorine gas access to the entire sample instead of just the surface or the polymer could simply be swelled in perfluorohexane to allow complete conversion.

A greater degree of analytical measurements on the polymer samples would also be of interest. Unfortunately, TGA and conductivity measurements on many of these samples could not be performed due to limited access to instrumentation. A correlation between the conductivity and swelling data of the polymers should give some interesting data showing both the difference in a partially fluorinated and perfluorinated material, as well as comparing the properties of the perfluorinated alternating copolymer prepared from VDF and the properties of a perfluorinated random copolymer prepared with TFE.

Attempts were made to obtain MALDI-TOF spectrum of the hydrolyzed copolymers of VDF and PSEPVE without success, likely due to the increased molecular weights and better packing. If these spectra could be obtained it would give better evidence on the nature of alternation of the polymer.

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Chapter 6

EVALUATION OF PERFLUOROPHOSPHINIC ACID SURFACTANTS FOR USE IN FINE POWDER PTFE PRODUCTION

6.1 Introduction to Fine Powder PTFE

The majority of fluoropolymers such as PTFE, FEP, PFA, PVDF, etc. are produced industrially using emulsion polymerization techniques.[1] Emulsion polymerizations have the benefit over solution polymerizations that water can be used as the solvent. Not only is water inexpensive, it also does not undergo chain transfer as do hydrocarbon solvents, allowing higher molecular weight polymers to be produced. In order to get hydrophobic monomers to dissolve in water, a surfactant is added that forms micelles, allowing the polymerization to take place within the micelles.

Industrial preparation of perfluorooctanoate (PFOA) has typically been carried out by two main routes, electrochemical fluorination and iodine telomerization of tetrafluoroethylene (TFE), with the latter being more common today, mainly due to the fact that 3M no longer produces the material.[2]

The surfactant capabilities of PFOA are exceptional due to the extremely hydrophobic perfluorinated tail combined with the water solubility of the ammonium carboxylate, where PFOA has a critical micelle concentration (CMC) of 28.6 mmol/L as determined by ^{19}F NMR spectroscopy.[3] Emulsion polymerizations of fluoropolymers have typically employed the use of PFOA as the emulsifying agent due to this low CMC and the ability for the polymerizations of fluorinated monomers to be carried out within the micelle. Additionally, as no hydrocarbon bonds are present, PFOA shows no chain transfer properties, allowing high molecular weight polymers to be produced.

Dispersion polymerizations are also commonly used in industry in the preparation of PTFE. A dispersion polymerization utilizes a surfactant similarly to emulsion polymerizations; however, the concentration of surfactant is below the CMC value so that an emulsion is not formed. The main reason for performing dispersion polymerizations is that it allows formation of small particles down to 0.10 micrometers in diameter, termed fine powder PTFE.[4]

Fine powder PTFE has two main advantageous properties over other forms of PTFE that make it an attractive material. First, it has a crystallinity of 96-98% despite also having an extremely high molecular weight. Secondly, fine particle PTFE can be turned into a paste by blending the polymer with a hydrocarbon lubricant to yield a material, allowing paste extrusion. This allows articles to be prepared from PTFE using paste extrusion, a common method used by engineers in industry. Without the use of fine particles, articles made of PTFE are typically prepared by simply machining the parts, an expensive route.[4]

After preparation of the object by paste extrusion, the volatile lubricant is removed and the material is sintered. Sintering causes the PTFE to recrystallize in whatever form it currently holds, having a final crystallinity of 50 - 60%. Extremely high molecular weight PTFE, estimated up to 50 million, is required to keep the crystallinity in this lower range. Lower molecular weight PTFE has less chain entanglement and a higher crystallinity than is desired in most final products.[4]

The typical conditions used for preparation of fine particle PTFE vary between different companies with different patent art and trade secrets. However, the basics involve adding a surfactant, such as PFOA, in a concentration below that of the CMC. An anticoagulant agent such as paraffin wax, which melts below the polymerization temperature, is added to keep the polymer dispersed throughout the reaction. Initiation is performed by persulfate salts or organic peroxides such as disuccinic acid peroxide in the temperature range of 0-95 ˚C. TFE pressures are held constant between 40 and 350 psi until the desired quantity of TFE has been consumed.[4] Workup is performed by diluting the latex to a desired density at a specific temperature, such as 1.074 g/mL at 48 ˚C. While stirring at 300 rotations per minute (RPM), 1.8 mL of 60% nitric acid is added to the latex until the polymer particles coagulate.[5] Care must be taken to not allow the PTFE particles above 19 ˚C after drying as this can lead to fibril formation, ruining the product. Fibrils are caused from PTFE particles coming into contact with sufficient force that a long thing strand of PTFE is pulled between them instead of only having small spheres. This phenomenon only occurs above 19 ˚C where the PTFE particles go from a triclinic to a hexagonal lattice.[1]

On May 16, 2000, the 3M company announced they would no longer prepare PFOA as it was becoming evident that PFOA accumulates in both the environment and mammals.[6] While acute toxicity is not seen with PFOA, which likely contributed to some of the lax regulatory controls on its disposal, it accumulates in the livers of mammals with a biological half-life of 4.37 years in humans.[6] Chronic effects have been reported with PFOA such as hormonal changes, slowed developmental effects, and carcinogenic effects.[7] These health concerns have led to a move to replace PFOA in the emulsion polymerizations of fluoropolymers, with the EPA requesting a 95% reduction in emissions of PFOA over the 10 year period between 2000 and 2010 and complete conversion to a new surfactant by 2015.

Due to the phase-out of PFOA, new emulsifying surfactants must be found that are more easily decomposed in the environment and have shorter biological half-lives. While a large effort has been placed on this by industry, DuPont alone has spent over $300 million on research and development in this area,[8] most of the research is kept in-house as trade secrets. Merck

KGaA (Darmstadt, Germany) has recently prepared a perfluorinated surfactant that they felt showed good promise as a candidate for replacing PFOA in fine powder PTFE production, but the company has no experience with TFE polymerizations. Therefore, the Thrasher group was brought in to begin investigating the preparation of fine powder PTFE using this new surfactant, bis(perfluorobutyl) phosphinic acid (MAFS-010).

6.2 Experimental

Merck Advanced FluoroSurfactant (MAFS-010) was used as received as a 50/50 weight percent solution in water (as received from Dr. Joe Twitchell, Merck KGaA). Ascarite II® and sulfate and phosphate salts were purchased from VWR and used as received.

6.2.1 Analysis of MAFS-010 by ^{31}P, ^{19}F, and ^{1}H NMR Spectroscopy

Verification of the structure and impurities of the material were done by dissolving MAFS-010 in D_2O and performing NMR spectroscopy using a 360 MHz Bruker NMR spectrometer for ^{19}F (see Figure 6.1) and ^{1}H spectroscopy and a 500 MHz Bruker NMR spectrometer for ^{31}P nuclei (see Figure 6.2).

$P^z(O)(OH)(CF_2^aCF_2^bCF_2^cCF_3^d)_2; P^y(O)(OH)_2(CF_2^aCF_2^bCF_2^cCF_3^d)$

^{19}F NMR spectrum of MAFS-010 in H_2O: δ^a -122.9 (2F, d: $J^{a,z}$ 83 Hz); δ^b -121.9 (2F, m); δ^c -127.1 (2F, t: $J^{c,b}$ 12 Hz); δ^d -82.3 (3F, t: $J^{d,c}$ 10 Hz).

^{31}P NMR spectrum of MAFS-010 in H_2O: δ^z 4.56 (q: $J^{z,a}$ 78 Hz); δ^y -2.13 (t: $J^{y,a}$ 78 Hz).

6.2.2 Determination of CMC by ^{19}F NMR Spectroscopy

Serial dilutions were performed of the surfactant by taking 1.00 mL stock solution and mixing with 1.00 mL DI water. From this solution, 1.00 mL is added to 1.00 mL DI water, and so on to produce five diluted solutions. These samples are analyzed by ^{19}F NMR spectroscopy

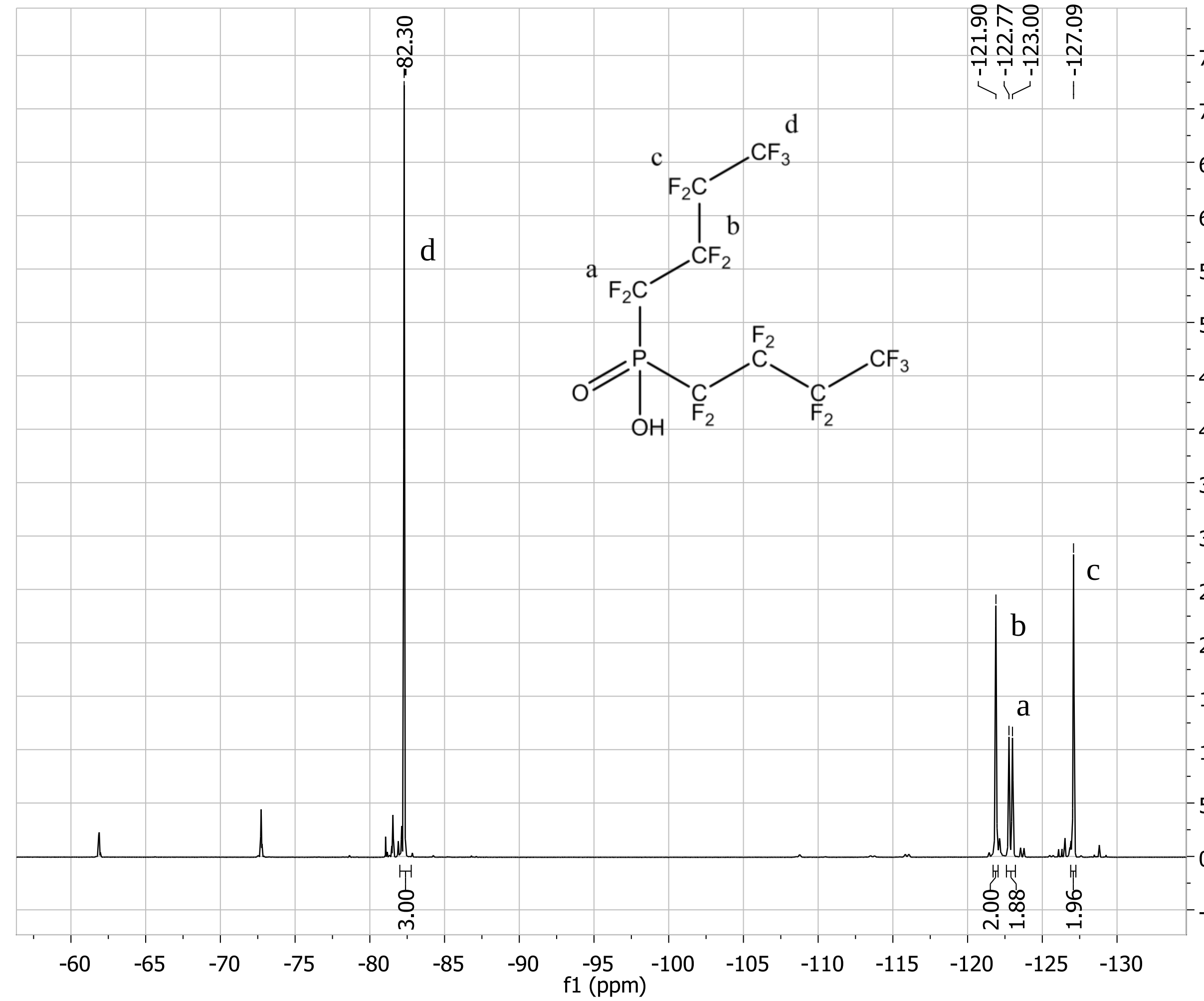

Figure 6.1 - ^{19}F NMR spectrum of MAFS-010 dissolved in H_2O.

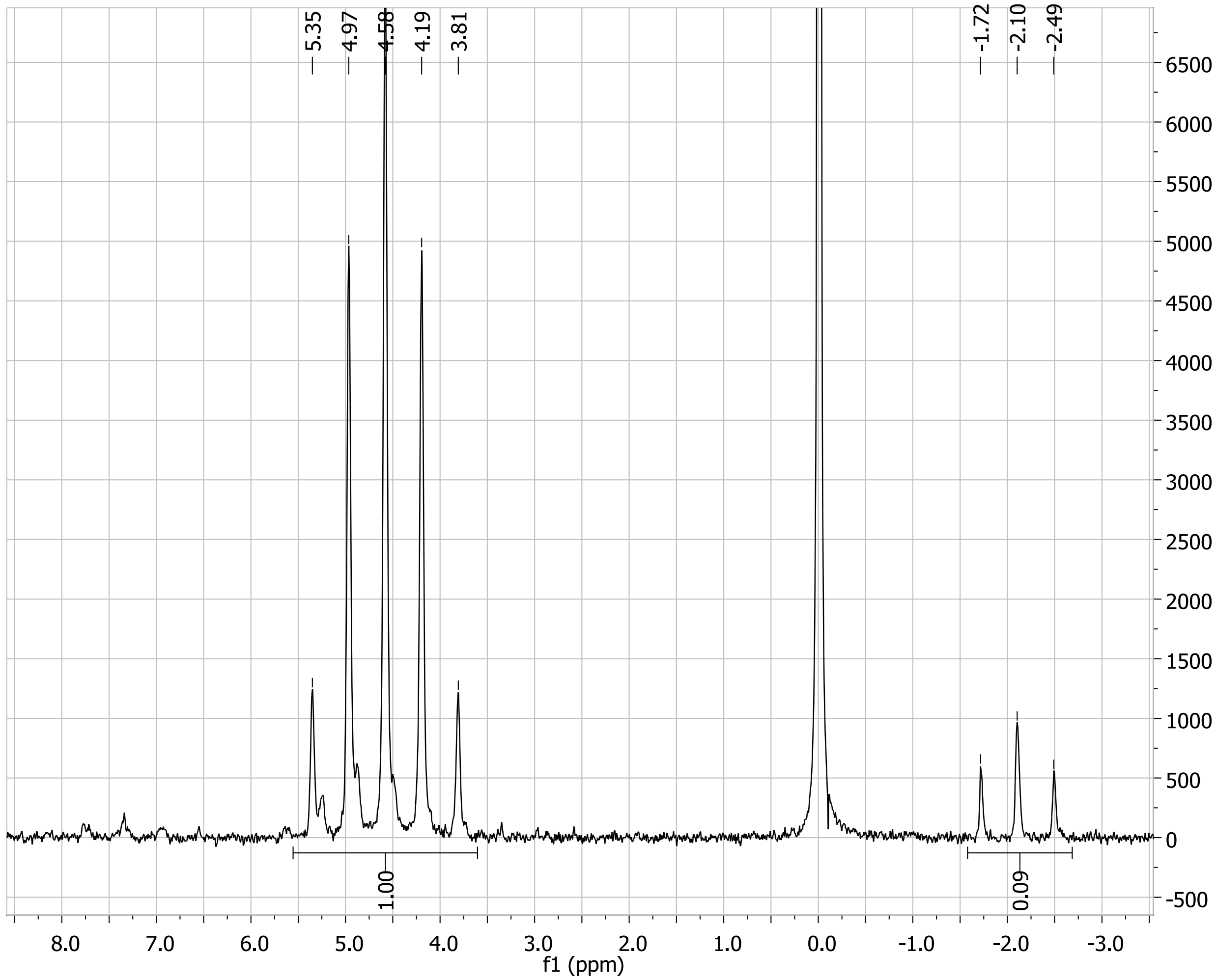

Figure 6.2 - ^{31}P NMR spectrum of MAFS-010 in H_2O. Phosphoric acid external standard added.

with a capillary containing 1% $CFCl_3$ in $CDCl_3$ inserted into the NMR tube. A plot of chemical shift versus the reciprocal of concentration is made, which gives two distinct lines of different slope, as seen in Figure 6.3. Additional solutions of known concentration in the vicinity of this intersection are then prepared and measured in order to give a more precise value of the CMC's. The CMC is determined to be 0.066 mol/L from the aforementioned plot.

6.2.3 Polymerization UAXMFG1 with MAFS-010

Similar to U.S. Patent 6,503,988, to a 600-mL stainless steel autoclave is added 197.06 mL of deoxygenated H_2O, 8.0431 g of paraffin wax with a melting point of 62 ˚C, and 1.34 mL of MAFS-010 stock solution, giving a final concentration of 7.23 mmol/L during the polymerization. The autoclave is sealed, taking care to keep oxygen out, and attached to the polymerization system as described in Chapter 1 before heating to 85 ˚C. A separate initiator solution of 1.1952 g of ammonium persulfate in 80.179 g of deoxygenated H_2O is prepared and added to a Teledyne-Isco HPLC syringe pump as described in Chapter 1. After deoxygenating the system by pressurizing with nitrogen and evacuating three times, TFE is slowly added with the Ascarite II® CO_2 scrubber in place, taking care that the temperature in the CO_2 scrubber never rises above 50 ˚C, to give a pressure of 117 psig at the autoclave. Using the syringe pump, 20 mL of the initiator solution is added to the autoclave using the HPLC pump and the pressure of TFE is kept constant at 117 psig while heating the polymerization at 85 ˚C overnight. Thereafter, the autoclave is removed from the system, and excess TFE pressure is vented into a fume hood. Coagulation is performed by stirring with an IKA T10 Basic Ultra-Turrax on the lowest setting and slowly adding 1.0 mL 15 M nitric acid until a solid precipitate begins to form. Less than 1 g of green solid is obtained, which gives an IR spectrum similar to virgin PTFE.

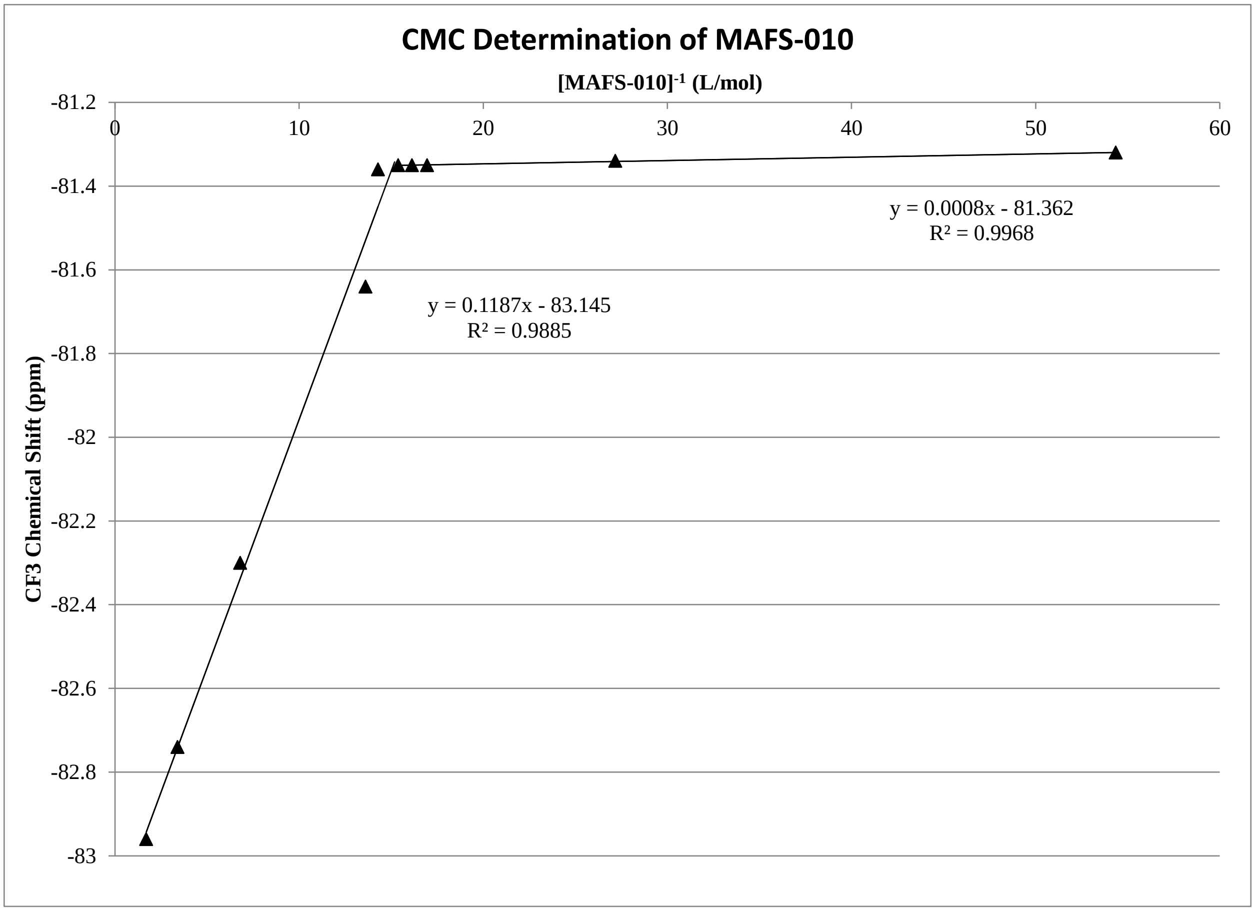

Figure 6.3. Plot of ^{19}F NMR chemical shift values for CF_3 group in MAFS-010 at varying concentrations.

6.2.4 Polymerization UAXMFG2 with MAFS-010

Similar to Example 6.2.3, to a 600-mL stainless steel autoclave is added 260 mL of deoxygenated H_2O, 2.97 g of disodium hydrogen phosphate heptahydrate, 1.45 g of sodium dihydrogen phosphate, and 11.786 mL of MAFS-010 stock solution. The autoclave is attached to the polymerization system, degassed, and heated to 85 ˚C. An initiator solution of 2.4983 g of ammonium persulfate in 112.06 g of deoxygenated H_2O is added to the HPLC pump. After slowly pressurizing the system up to 150 psi neat TFE, 35.0 mL of the initiator solution is added to the autoclave using the syringe pump. No significant pressure drop was observed. Workup is performed similarly to Example 6.2.3, which gave less than 0.5 g of solids.

6.2.5 Polymerization UAXPFG1 with PFOA

To a 100 mL stainless steel autoclave is added 0.678 g of PFOA, 0.859 g of disodium hydrogen phosphate heptahydrate, 0.498 g of sodium dihydrogen phosphate, and 30 mL of degassed H_2O. The autoclave is attached to the polymerization system as before and heated to 85 ˚C. After slowly pressurizing the system up to 100 psi of neat TFE, 20.0 mL of a 39.1 mmol/L solution of ammonium persulfate in deoxygenated H_2O is added. The polymerization is allowed to proceed overnight at which point workup is performed similarly to Example 6.2.3, yielding 380.4 mg of polymer with an IR spectrum similar to that of PTFE.

6.2.6 Copolymerization of PSEPVE and TFE with MAFS-010 (UAXMR1)

Similarly to the emulsion polymerization in Example 2.2.12, to a 600-mL stainless steel autoclave is added 2.44 mL of stock MAFS-010, 8.465 g of PSEPVE, 0.7213 g of $NaHSO_3$, 3.9842 g of $NaH_2PO_4 \cdot H_2O$, 6.8543 g of Na_2HPO_4 and 350.06 g of deoxygenated H_2O. The autoclave is attached to the polymerization system as before and heated to 60 ˚C. After slowly pressurizing the system to 60 psi of neat TFE, 50.0 mL of a 0.110 M solution of ammonium persulfate in deoxygenated water is added to the system using the syringe pump and the reaction is allowed to proceed overnight. After disconnecting the autoclave from the system and venting the unreacted TFE pressure in a fume hood, workup is performed by adding 12 M HCl until micelle disruption causes precipitation of the product. No product was obtained.

6.2.7 Copolymerization of Dow and TFE with MAFS-010 (UAXMD1)

Similarly to Example 6.2.3, to a 600 mL stainless steel autoclave is added 4.88 mL of stock MAFS-010, 9.264 g of Dow vinyl ether, 0.7078 g of $NaHSO_3$, 3.9833 g of $NaH_2PO_4 \cdot H_2O$, 6.8758 g of Na_2HPO_4 and 350.16 g of deoxygenated H_2O. The autoclave is attached to the polymerization system as before and heated to 60 ˚C. After slowly pressurizing the system to 60 psi neat TFE, 50.0 mL of a 0.110 M solution of ammonium persulfate in deoxygenated water is added to the system using the syringe pump, and the reaction is allowed to proceed overnight. After disconnecting the autoclave from the system and venting TFE pressure in a fume hood, it was observed that a similar quantity of Dow monomer as was added is present in the bottom of the solution, suggesting the monomer is not incorporated within the micelles during polymerization. No solid polymer product was obtained.

6.2.8 MAFS-010 Radical Stability Test

To a vial containing 1.000 mL of stock MAFS-010 under a nitrogen atmosphere is added 23.9 mg ammonium persulfate. The solution is heated overnight at 85 ˚C, at which point the solution is analyzed by ^{31}P and ^{19}F NMR spectroscopy.

6.2.9 MAFS-010 Thermal Stability Test

A vial containing 1.000 mL of stock MAFS-010 under a nitrogen atmosphere is heated overnight at 85 ˚C, at which point the solution is analyzed by ^{31}P and ^{19}F NMR spectroscopy.

6.2.10 Scanning Electron Microscope Image of UAXPFG1

Imaging of the polymer produced from polymerization UAXPFG1 is performed using a JEOL-7000 field emission scanning electron microscope (SEM). An accelerating voltage of 1.0 kV is used to obtain an image with a magnification of 650x with a 10 micrometer scale bar.

6.3 Results and Discussion

Initial characterization of MAFS-010 by NMR shows the material to be approximately 85% bis(perfluorobutyl) phosphinic acid, 10% perfluorobutyl phosphonic acid, and 5% phosphorus containing byproducts which were not characterized further.

Determination of the CMC of MAFS-010 is performed similarly to the method employed by DesMarteau and co-workers in the CMC determination of a sulfonimide monomer.[3] The CMC is considered as the point where half the surfactant molecules are present in the micelle form. While different theories exist for CMC determination, the mass action model will be used here, where free surfactant molecules in solution are considered as different molecules from surfactant molecules in micelles. Plotting the chemical shift of the surfactant functional groups verse the reciprocal of the concentration allows two different best fit lines with distinct slopes to be plotted. The intersection of these two lines, which in this model are considered two different species, shows the point where the surfactant molecules switch from freely dispersed to micelles.

Here, the CF_3 functional group is shown to have the largest change in chemical shift as the concentration is lowered, and it is used for the CMC determination. Two distinct best fit lines can be found that intersect at a concentration of 66.2 mmol/L. This value is higher than the CMC for PFOA, 16.7 mmol/L,[3] calculated by the DesMarteau group suggesting a larger amount of surfactant would be required for polymerizations. Without knowledge of the technical requirements needed for a PFOA replacement it is not known by the authors whether this higher CMC is acceptable as a PFOA replacement or not.

Fine powder PTFE production was performed similarly to Example 1 from U.S. Patent 6,503,988.[5] This method was settled on based upon presenting the polymerization and workup conditions as well as the lower TFE pressures versus many other methods.[4] These lower pressures were considered important for increased safety as CO_2 was removed from the TFE, adding the risk of deflagration. As the homopolymerization of TFE has been shown to be sufficiently exothermic to cause deflagration, the use of lower TFE pressures to decrease the rate of polymerization is beneficial for early polymerizations to researchers who are unfamiliar with PTFE production.

Two fine powder PTFE polymerizations were attempted with MAFS-010 as the surfactant and one with PFOA. None of the three polymerizations would be considered a success as no more than 1 g of PTFE was produced in any of the polymerizations. Typically the latex from these dispersion polymerizations goes to 30 weight percent solids or more, so 1.0 g of product from around 200 g water is far from these results. While the failure of the polymerizations with MAFS-010 could be blamed on the chain transfer properties of the surfactant, *vida infra,* the failure of the polymerization using PFOA cannot use such an excuse. This suggests the failures were likely due to lack of experience with these types of polymerizations by the researchers.

SEM imaging, shown in Figure 6.4, is performed on the product obtained from polymerization UAXPFG1. Comparing these images to literature SEM images of fine powder PTFE shows the resin produced here does not contain particles of a narrow size distribution and particles are larger in size, roughly 2-4 micrometers in diameter, compared to the literature.[4]

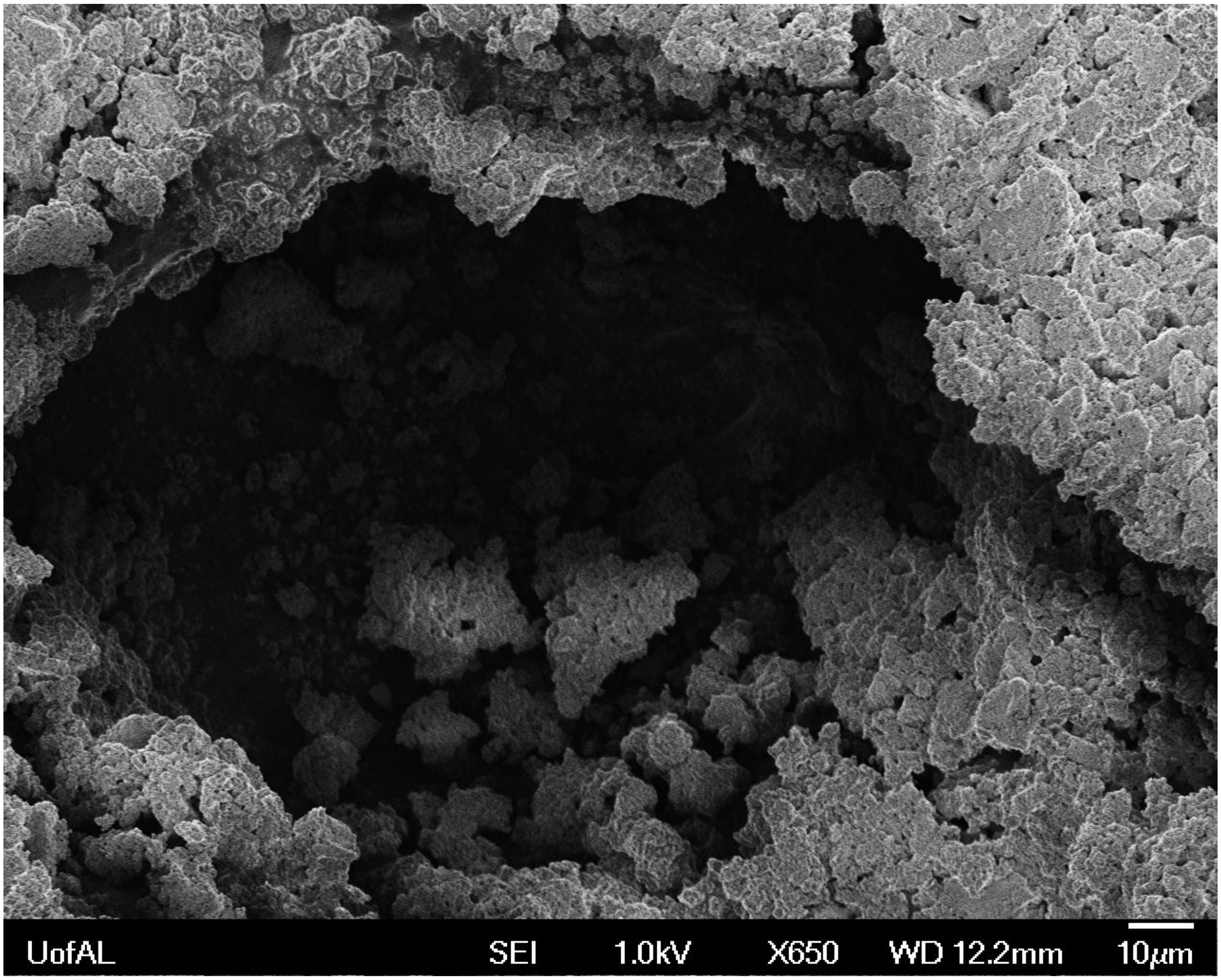

Figure 6.4. SEM image of UAXPFG1 at 650x.

Two additional polymerizations of copolymers of TFE with PSEPVE and Dow were performed similarly to those done in Chapter 2. The only difference in these two polymerizations with those performed in Chapter 2 is the use of MAFS-010 instead of PFOA. The amount of surfactant used for UAXMR1 is in a similar excess as the PFOA used previously based on the CMC. No polymer is recovered from the reaction using similar conditions as have been found to work with PFOA as the surfactant.

It was hypothesized the failure of the emulsion copolymerization of TFE and PSEPVE with MAFS-010 could be due to the altered micelle structure not favoring incorporation of PSEPVE inside the micelles. As the fluorocarbon chains on MAFS-010 are only 4 carbons long as opposed to 7 carbons long on PFOA, a different micelle structure is expected. Incorporation of the Dow monomer with a shorter side chain may alleviate this problem. Additionally, use of twice as much MAFS-010 surfactant was employed in UAXMD1. However, during workup it was noticed that almost all Dow monomer was in a second layer and not incorporated in the micelles.

Due to the failures to obtain product from these polymerizations, including the copolymerization of TFE and PSEPVE that had previously worked well with PFOA as the surfactant, tests were done to determine the stability of the surfactant under the temperatures and radical conditions present in the polymerization. Heating the surfactant to 85 ˚C overnight under a nitrogen atmosphere shows no decomposition by ^{31}P or ^{19}F NMR spectroscopy suggesting that it is thermally stable under these conditions.

The radical stability of the surfactant was determined by placing 1.000 mL of stock MAFS-010 in a vial with 23.9 mg of ammonium persulfate, a similar concentration of initiator to surfactant as used in the polymerizations, and heating the mixture at 85 ˚C overnight. Analysis by ^{31}P NMR spectroscopy, as seen in Figure 6.5, shows that the phosphinic acid has been decomposed predominately to phosphonic acid with some phosphoric acid as well. Based on integrations the resulting mixture is 25% phosphinate, 64% phosphonate, and 11% phosphate compared to the original MAFS-010 solution that is 89% phosphinate, 11% phosphonate, and 0% phosphate not accounting for the other impurities within the MAFS-010 sample.

This decomposition occurs from a chain transfer of the initiator radical to phosphorus, yielding a perfluorobutyl radical and adding a hydroxyl group to the phosphinate or phosphonate. The high rate of chain transfer for this surfactant shows its inability to be useful as a PFOA replacement in PTFE production, at least under the conditions that were attempted. Molecular weights of PTFE need to be in the range of millions to tens of millions grams per mole, which can only be accomplished by having a very low rate of termination. Having a surfactant which can terminate the growing PTFE polymer chains through a chain transfer reaction would significantly increase the rate of termination and yield unacceptably low molecular weight polymer chains. Due to this chain transfer mechanism, it was decided that MAFS-010 is not an acceptable candidate to replace PFOA in the application of fine powder PTFE suspension polymerization, unless more appropriate conditions are found by which to minimize chain transfer.

6.4 Conclusions and Future Work

A new perfluorinated surfactant has been tested for its use in the preparation of fine powder PTFE. While the researchers are not highly skilled in this type of polymerization and an attempt with PFOA was not successful, no positive results were obtained for any polymerizations with the new surfactant. Stability tests of the surfactant towards free radical initiators were

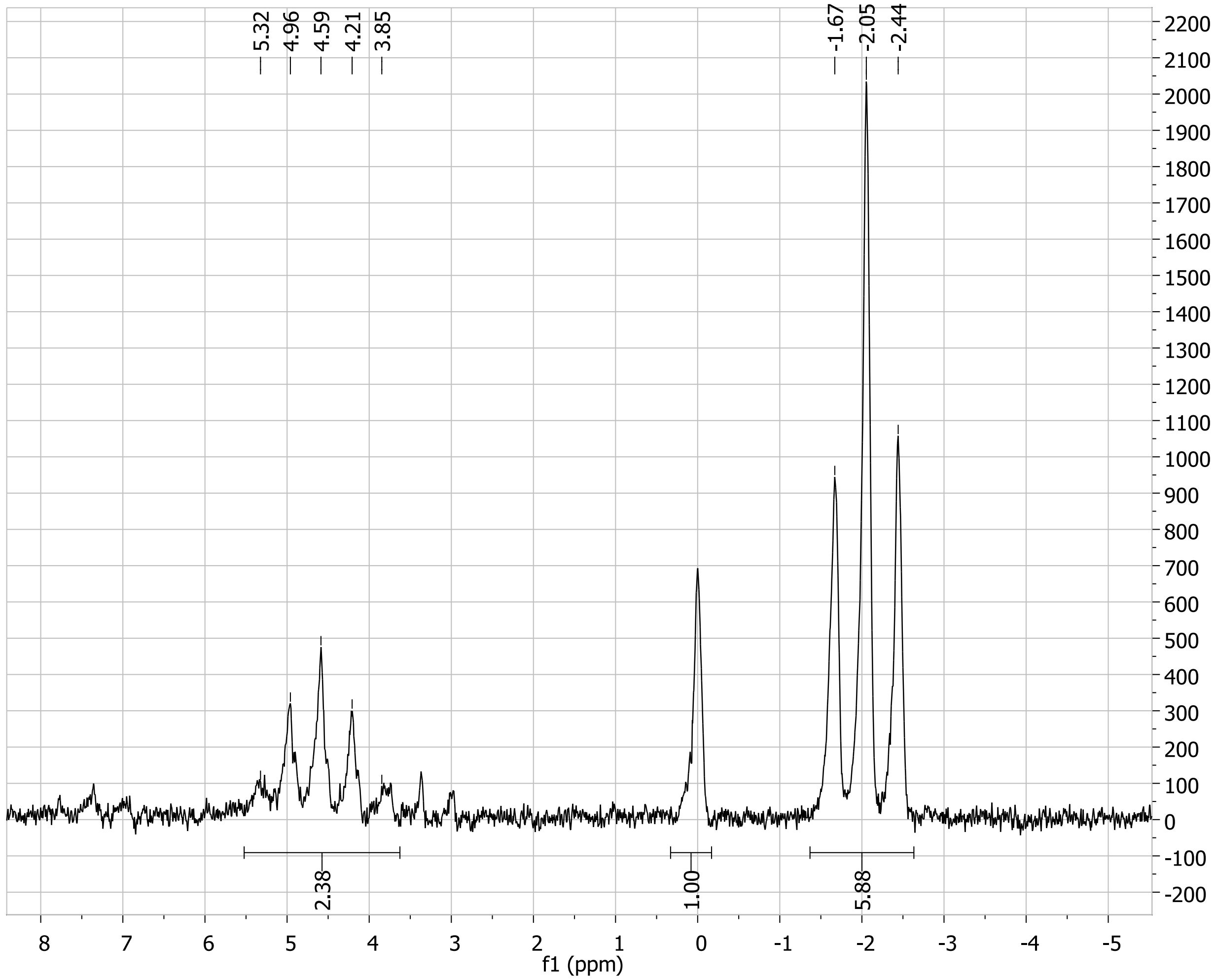

Figure 6.5 - ^{31}P NMR spectrum of MAFS-010 dissolved in H_2O after overnight with ammonium persulfate radical initiator.

attempted which showed the surfactant does indeed chain transfer, limiting its usefulness in the preparation of high molecular weight fluoropolymers.

Future work in this area should first focus on finding an appropriate synthesis of fine powder PTFE using PFOA and this polymerization system. While fine powder PTFE is commonly prepared in industry, much of the information is kept as trade secrets and involves reactors different from the 600 mL autoclave used here. Finding the right conditions to produce fine powder PTFE using this system would allow the same conditions to be attempted with new surfactants to better determine if an inability to prepare the polymer is due to the method or the new surfactant. Additionally, the ammonium salt of MAFS-010 should be prepared and tested for its stability towards chain transfer and applicability as a surfactant in polymerizations.

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