

SYNTHESIS AND CHARACTERIZATION OF WATER INSOLUBLE COPOLYMERS
FROM DIALLYLDIMETHYLAMMONIUM HEXAFLUOROPHOSPHATE

by

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A thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Doctor of Philosophy (Applied Chemistry).

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ABSTRACT

Poly(diallyldimethylammonium chloride) (PDADMAC) is a cationic, water-soluble polymer important for numerous industrial applications. The polymer is prepared through the radical cyclopolymerization of diallyldimethylammonium chloride (DADMAC) in water or other polar solvents. Copolymerization has traditionally been accomplished with water-soluble comonomers to alter the copolymer properties. However, the inherent water solubility of DADMAC polymers prevent the materials from being used as water resistant films and membranes. The work herein seeks to develop DADMAC copolymers that incorporate the cationic moiety and hydrophobic components for use as water insoluble materials. This research exploits the discovery that DADMAC monomer and PDADMAC polymers can be made water-insoluble by anion exchange of the chloride counterion to that of the hydrophobic hexafluorophosphate (PF_6). The resulting PF_6 salt form further makes the monomer or polymers organic soluble, allowing copolymerization with hydrophobic monomers in polar aprotic solvents. Two distinct approaches were pursued in this research: (1) radical copolymerization of DADMA(PF_6) monomers with hydrophobic comonomers; (2) step growth copolymerization of end-functional PDADMA(PF_6) oligomers to make multiblock copolymers. Copolymers of DADMA(PF_6) and methyl methacrylate were synthesized via a radically initiated bulk polymerization. The copolymers were successfully synthesized over a range of comonomer feed ratios, and, at high conversion, excellent incorporation of both monomers was observed. The resulting cationic copolymers cast free-standing films that were entirely insoluble in water. To produce block copolymers, telechelic PDADMA(PF_6) oligomers were synthesized using functionalized reagents that act as radical initiators, chain transfer agents, and terminators (iniferters). Based on the functionality, the oligomers were suitable for incorporation as blocks into polysulfones, aromatic polyamides, and polyimides. The relative amounts of the PDADMA(PF_6) in all types of block copolymer was tuned by changing the monomer feed ratio. While all copolymers formed water insoluble, free-standing films, their properties were closely tied to both the backbone functional groups and composition. Preliminary characterization demonstrates that the new materials have the potential in applications as modified polyelectrolyte films and membranes.

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ACKNOWLEDGEMENTS

I would like to thank Dr. Dan Knauss for being an invaluable research advisor and mentor whose support motivated me to both begin and complete my Ph.D. work. I am very grateful to my group members, Sal Fruciano and Daniel Frazier, for all the help they have provided me. I am deeply indebted to Dr. Yuan Yang and Ed Dempsey for the many times their skills and expertise were essential to my research. To the members of my thesis committee, Dr. Alan Sellinger, Dr. Dylan Domaille, and Dr. Ning Wu, I am thankful for the important advice and feedback. I extend my appreciation to Dr. Tom Gennett, Samuel Nez, and Megan Rose, for the immense amount of work they did to support the chemistry department and its students for both my graduate and undergraduate career. I would like to thank Ramona Figueroa for her assistance and for teaching me how to work in a lab. Finally, my gratitude goes to my friends, roommates, family, and loved ones who have provided me with endless kindness and motivation over the course of my studies.

CHAPTER 1

RECENT ADVANCES IN THE SYNTHESIS OF DIALLYLAMMONIUM POLYMERS

Alison Biery¹ and Daniel Knauss¹

1.1 Abstract

Diallyldimethylammonium chloride (DADMAC) and its polymer (PDADMAC) have been widely studied and used over the past six decades due to the high charge density of ammonium groups, good chemical stability, facile synthesis, and low toxicity of the materials. The incorporation of DADMAC into a variety of copolymers has allowed for modification of properties and increased potential applications. Since the publication of a comprehensive review of PDADMAC in 1999, the interest in DADMAC and related monomers has continued to grow, and many studies of novel polymerization systems have been recorded. The novel structures investigated include water soluble cationic and zwitterionic copolymers as well as amphiphilic and hydrophobic copolymers. While DADMAC is the most common diallylammonium monomer, other similar monomers have been studied, including diallyldimethylammonium with other counterions, guanidinium-based molecules, and diallyl heterocycles, which has led to the formation of spirocyclic polymers. This review will focus on recent advances in the synthesis of novel DADMAC containing polymers and copolymers, as well as the polymers and copolymers from similar diallylammonium monomers.

1.2 Introduction

As fields like biotechnology and energy storage continue to evolve, there is an ever-increasing need for advanced polyelectrolyte materials. Cationic polyelectrolytes are of interest for applications including anion exchange membranes, antibacterial coatings, gene delivery systems, and water purification.^{1,2} Of the possible cationic moieties, quaternary ammonium groups are the most common.³ Quaternary ammonium polymers can be synthesized through the polymerization of cationic monomers, the polymerization of amine monomers followed by quaternization, or the polymerization of a monomer with suitable functionality to which a

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pendant ammonium can be attached. Polymers containing the ammonium functionality are known to have high charge density, tunability, and thermal and chemical stability.

In the 1950s, Butler and coworkers at the University of Florida polymerized diallyldimethylammonium bromide (DADMABr) with peroxide initiators in an attempt to produce a cross-linked network⁴ based on the principle that the polymerization of unconjugated dienes leads to the formation of nonlinear, cross-linked polymers.^{5,6} Unexpectedly, the resulting polymers were found to be water soluble and contain no cross-linking. Further examination determined that the resulting polymer structure was comprised of linear chains of intramolecularly cyclized monomer.⁷ In the following decades, kinetic, fragmentation, and degradation studies confirmed that the polymerization proceeded through a series of alternating intra- and inter-molecular chain propagations.⁸ The unique mechanism, now known as cyclopolymerization, is the understood polymerization for a range of divinyl, allyl-vinyl, and diallyl monomers.⁹ While it was initially suspected that the backbone of polydiallyldimethylammonium was comprised of six-membered rings, nuclear magnetic resonance (NMR) spectroscopy studies concluded that the enchainment exists mostly as five-membered rings (Figure 1.1).^{10,11} Although the original polymerization used the bromide counterion form of the monomer, it was soon discovered that diallyldimethylammonium chloride (DADMAC) is kinetically more reactive to polymerization.¹² Since this discovery, the homopolymer PDADMAC has become increasingly common.

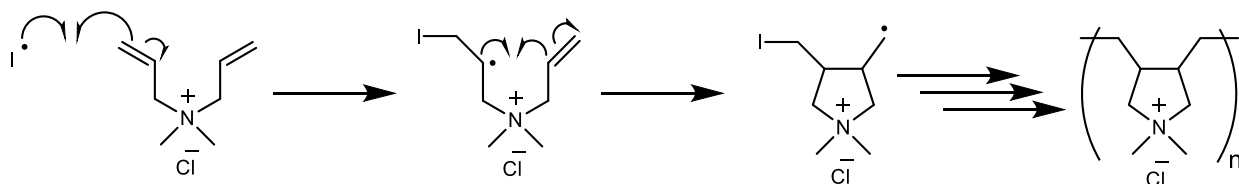


Figure 1.1 The cyclopolymerization of DADMAC.

The cyclopolymerization formation of PDADMAC imparts it with unique properties. The repeating quaternary ammonium groups give it a high permanent charge density and water solubility. While the electron deficient sites of many polycations are highly susceptible to nucleophilic attack, the pyrrolidinium-type cations of PDADMAC are sterically hindered and contain no labile carbon-nitrogen bonds. As a result, PDADMAC has significantly higher base stability than pendant ammonium polycations.¹³ The beneficial properties of PDADMAC make it

an important polymer for several industrial-scale applications. The first industrial application of PDADMAC was to provide conductivity in specialty papers¹⁴ and it has maintained an important role in the paper and textile industries.^{15–19} However, the largest use of PDADMAC is in wastewater treatment. PDADMAC interacts electrostatically with the surface of negatively charged water contaminants, which neutralizes the anionic material and causes it to coagulate into larger particles that sediment out of solution in a process known as flocculation.²⁰ PDADMAC was the first polymer approved by the FDA for use in the treatment of potable water²¹ and is still widely used today.^{22–25} Due to its high charge density, the homopolymer is useful as a polyelectrolyte.^{3,26–29} PDADMAC is a common component of cosmetics and cleaning products because it is both antibacterial and nontoxic.^{30–32} In addition, the synthesis of copolymers incorporating DADMAC units expanded the properties and application of the polymer. As a result of both its unique synthetic mechanism and industrial usefulness, PDADMAC has been extensively investigated.

In 1999, Wandrey, Hernández-Barajas, and Hunkeler published a comprehensive review of the synthetic techniques for the preparation of PDADMAC employed up to that time, as well as discussions of copolymerizations, kinetic studies, and applications of the polymer.¹⁴ However, a significant amount of research involving DADMAC polymerization has been completed in the following years. While some additional reviews have covered the topics of cyclopolymerization^{6,33} or quaternary ammonium polymers,³ there has not been a comprehensive review of DADMAC containing polymers since 1999. This review will focus on novel polymerizations incorporating the DADMAC monomer. Techniques in the synthesis of PDADMAC will be discussed, with a special focus on the reports of controlled/living polymerizations. Recent research on linear copolymers of DADMAC with a variety of hydrophilic and hydrophobic comonomers will be covered. The last two sections will move beyond DADMAC to discuss some important polymerizations of diallyldimethylammonium monomers with non-chlorine counterions and other structures of diallyl cationic nitrogen monomers.

1.3 Novel Techniques for the Synthesis of Homo-PDADMAC

PDADMAC is typically obtained through traditional radical polymerization. Polymerization of DADMAC has been carried out in organic solvents like acetone, *N*-methyl-2-

pyrrolidone, trimethylurea, and dimethylformamide.¹⁴ However, the polymer is only substantially soluble in water, methanol, and acetic acid, so polymerizations in aqueous media are the most common. Because large-scale PDADMAC polymerizations are often carried out in homogenous systems, water soluble radical initiators are often employed. *Tert*-butyl hydroperoxide was used as the redox initiator in the original cyclopolymerization works.^{4,8} In the following years, a variety of peroxide, azo, and persulfate compounds were shown to successfully initiate the polymerization of DADMAC.³⁴ Ammonium persulfate has become the preferred initiator for DADMAC polymerizations because persulfate ions are reported to favorably interact with the ammonium groups in the PDADMAC backbone, which can both increase the decomposition rate of the salt to active initiator and stabilize the forming polymer.³⁵ Suggested temperatures and monomer concentrations for the traditional radical polymerization of DADMAC vary from 30-80 °C and 10-70 wt. %.³⁴ Initiator concentration is also variable depending on the initiator identity and desired average molecular weight. Although traditional radical polymerization is the most common method for producing PDADMAC, ionic and X-ray induced polymerization have been investigated.³⁶ More recently, techniques have been studied to produce PDADMAC with a focus on increasing control over end groups and chain length.

1.3.1 Controlled Radical Polymerization

Controlled radical polymerizations have been developed over the last few decades to approach the level of control previously only known for living anionic and cationic polymerizations. Several techniques have been studied, including nitroxide mediated polymerization (NMP),³⁷ atom transfer radical polymerization (ATRP),³⁸ and reversible addition-fragmentation chain transfer (RAFT) polymerization.³⁹ While each technique has unique advantages and drawbacks, RAFT can be performed in a wide variety of solvents, including water.⁴⁰ RAFT polymerization relies on the addition of a thiocarbonyl RAFT agent to a radical polymerization system. The RAFT agent reversibly adds to the end of the growing polymer chains to produce an equilibrium of growing radical chains and dormant capped chains.³⁹ Since the rate of reversible transfer of the end-group between the growing and dormant chains is higher than the initiation rate, all chains have a similar degree of polymerization, leading to a narrow molecular weight distribution. The functionalized chain-ends resulting from a RAFT polymerization maintain their reactivity so that the addition of a new batch of monomer will lead to extension of the polymer chains without the need for additional initiator. Shortly

after Chiefari et al. discovered RAFT in 1998,⁴¹ it became the favored technique for controlled radical polymerization in aqueous media and has remained the most facile technique. As a result, RAFT polymerization is particularly well studied for the polymerization of charged monomer species. The first report of the RAFT polymerization of a charged monomer, 4-styrenesulfonate, in an aqueous system was published in 2001.⁴² Since then, RAFT has been expanded to the synthesis of a variety of cationic polymers, including those with ammonium groups.

Many investigations of the RAFT polymerization of DADMAC have been carried out by the Agarwal group. Their first study examined both 3-benzyltrithiocarbonyl propionic acid (trithiocarbonate) and ethylxanthogenacetic acid (xanthate) RAFT agents (Figure 1.2) with ammonium persulfate employed as an initiator.⁴³ In addition to changing RAFT agent identity, the effect of reaction temperature and the concentration of RAFT agent were modified to optimize the extent of control. The success of the RAFT polymerization was determined by analyzing percent monomer conversion, molecular weight distribution, and capacity to undergo chain extension upon the addition of new monomer. The xanthate RAFT agent demonstrated relatively poor control. Though PDIs as low as 1.12 were achieved, the molecular weight of the polymers only increased up to three hours, but no further growth occurred over the next four hours despite the presence of unreacted monomer. Additionally, PDADMAC chains produced with the xanthate agent could not undergo further chain extension. In contrast, PDADMAC synthesized using the trithiocarbonate RAFT agent demonstrated a linear increase in molecular weight over the course of the reaction. Increasing the concentration of RAFT agent with respect to monomer led to chains of lower molecular weight, which is an expected trend for RAFT polymerizations. The introduction of new monomer to chains capped with an active trithiocarbonate unit displayed an increase in number average molecular weight from 17,200 to 30,000 g/mol. When the reaction temperature for the trithiocarbonate system was increased from 60 to 90 °C, polydispersities increased from 1.15 to 1.41, which may indicate some control is lost at higher temperatures. The results of this study support the potential of using RAFT techniques for the cyclopolymerization of DADMAC under the appropriate conditions. However, the trithiocarbonate RAFT polymerization was relatively slow and required 24 hours to achieve approximately 86 % conversion. When microwave assisted polymerizations were carried out with the trithiocarbonate RAFT agent, 80 % conversion was reached at five hours while PDI remained below 1.2.⁴⁴ The PDADMAC produced from the microwave-assisted RAFT

polymerization could undergo chain extension with the introduction of new DADMAC, which demonstrates that the microwave synthesis did not interfere with the polymerization control.

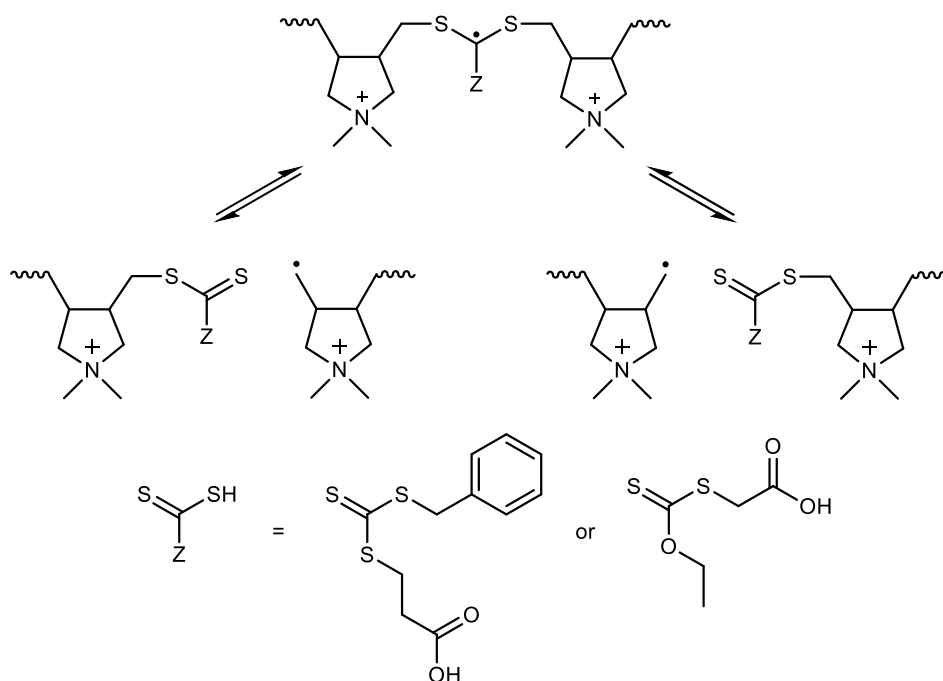


Figure 1.2 RAFT polymerization of DADMAC with trithiocarbonate or xanthate RAFT agents. Chloride counterions omitted for clarity. Adapted from ref. 43.

However, in a 2011 paper, the Agarwal group concluded that that the controlled character of the DADMAC/trithiocarbonate polymerization was not as significant as originally thought and was limited to low conversions.⁴⁵ In a series of polymerizations using 2,2'-azobis(2-methylpropionamide) dihydrochloride as initiator and 2-(Dodecylthiocarbonothioylthio)propanoic acid as RAFT agent, molecular weight was found to increase linearly up to 20 % conversion while low PDI was maintained. Higher molecular weight and conversions were reached only with a dramatic increase in polydispersity (up to 2.8). The increase in polydispersity at high conversion indicates that while some control can be accomplished early in the RAFT polymerization of DADMAC, all the characteristics of a well-controlled RAFT polymerization were not achieved.

At the same time as the Agarwal studies, the Wilson group was attempting a controlled polymerization of DADMAC using the macromolecular design by interchange of xanthate (MADIX) RAFT technique. The initial polymerization employed a hydrophobic xanthate RAFT

agent in a water/ethanol solution,⁴⁶ which was problematic due to the frequency of chain transfer to ethanol. To reduce the rate of chain transfer, a controlled radical polymerization was performed to produce an oligomer with an average of 7.2 (as indicated by NMR spectroscopy) acrylamide repeat units capped with the RAFT agent (Figure 1.3). Since the acrylamide species is more water soluble than the RAFT agent alone, the polymerization could be performed in a lower concentration of ethanol, reducing the chain transfer to solvent. The resulting PDADMAC chains produced using the acrylamide oligomer RAFT agent contained a short polyacrylamide cap at one end from the initiating group. In direct contrast to the xanthate mediated polymerization results seen in the first study from the Agarwal group,⁴³ the polymers exhibited linear molecular weight growth over time. However, the reported PDIs were relatively high (1.8-2.3), and all polymers synthesized were under 30,000 g/mol. The same technique was also found to produce block copolymers using higher molecular weight polyacrylamide initiator segments followed by the polymerization of PDADMAC blocks. The results are further indication that some control is possible using RAFT polymerization, but the combination of high molecular weight and low dispersity is not easily achieved.

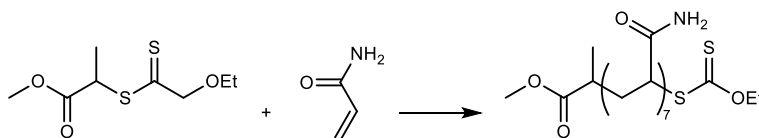


Figure 1.3 Oligomeric polyacrylamide RAFT agent. Adapted from ref. 46.

A similar technique was investigated to produce polystyrene copolymers. To prepare a diblock copolymer, RAFT polymerization of DADMAC was done using the ethylxanthogenetic acid as chain transfer agent to form blocks. The functionalized end-groups of the oligomeric PDADMAC was then used to initiate the polymerization of styrene.⁴⁷ Two diblock copolymers were synthesized, one with PDADMAC and PS blocks of equal molecular weight (17 kg/mol) and one with a shorter PDADMAC than PS block (8 and 32 kg/mol) as determined by NMR spectroscopy. Linear molecular weight growth was reported up to approximately 80 % conversion of PS and the PDIs of the PDADMAC block and the 17 kg/mol diblock copolymer were found to be 1.20 and 1.75, respectively. In 2020, a similar polymer system was synthesized using mono and difunctional RAFT agents made of short oligomers of polyacrylamide capped with ethylxanthogenetic acid on either one or both ends.⁴⁸

Polymerization of DADMAC by the oligomeric RAFT agents were carried out in aqueous solution and chain extension with styrene was performed in an emulsion polymerization such that latex particles formed (Figure 1.4). In the initial aqueous polymerization of DADMAC, linear molecular weight growth was observed up to approximately 70 % where conversion suddenly ceased. For the monofunctional RAFT agent, PDIs as low as 1.12 were reported at low conversion. As conversion increased, PDADMAC polydispersity generally did as well until reaching 1.51 at the conversion cap. The increase in molecular weight distribution and limited conversion leaves some question as to the validity of RAFT polymerization of DADMAC.

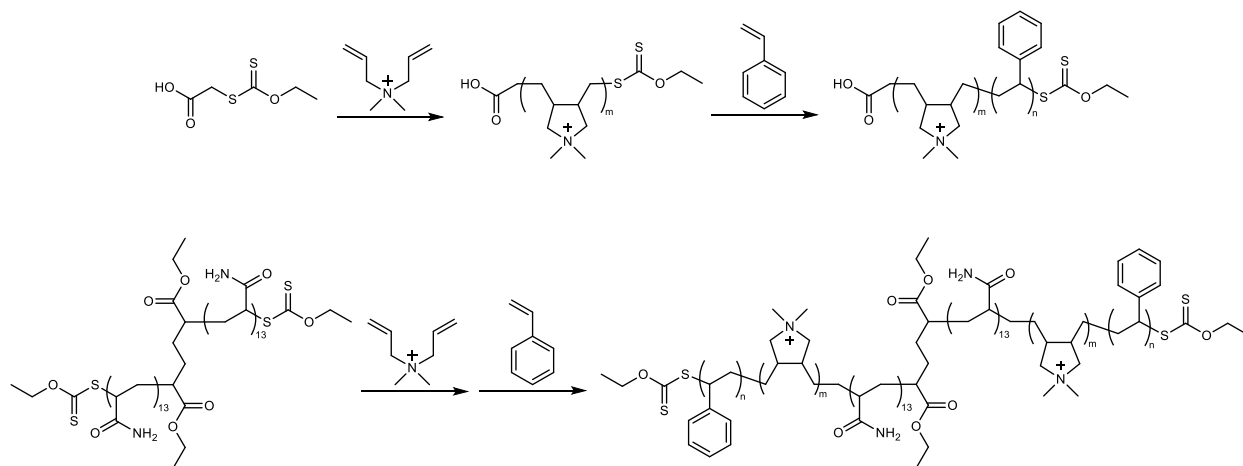


Figure 1.4 RAFT synthesis of PDADMAC-*block*-PS latex particles. Chloride counterions omitted for clarity. Adapted from ref. 48.

RAFT-based DADMAC polymerization has also been studied as a method for surface modification by grafting. Graphene oxide sheets were functionalized with 2-bromopropionyl bromide then exposed to potassium O-ethyl xanthate to produce a functionality that served as a RAFT initiator for PDADMAC grafting.⁴⁹ Grafting was confirmed by IR and NMR spectroscopy and the presence of polymer resulted in increased thermal stability of the graphene sheets as confirmed by TGA and DSC. Molecular weight and polydispersity of the PDADMAC chains were not characterized, making it difficult to determine the level of control achieved. The PDADMAC grafted graphene oxide was then used to produce nanocomposite polysulfone membranes that demonstrated good metal, salt, and dye exclusion as well as better water flux, water uptake, hydrophilicity, and antifouling than standard polysulfone membranes. There have not been consistent results demonstrating good control and the results vary significantly between reports. Further investigations into the controlled radical polymerization of DADMAC will be

necessary before RAFT polymerization can be accepted as a viable technique for the synthesis of complex DADMAC copolymers.

There is also interest in the modification of metallic surfaces by grafting, particularly to transform surface characteristics like hydrophobicity. To prepare aluminum plates for grafting, they were soaked in aqueous monochloroacetic acid or methanolic 3-chloromethylbenzoic acid to form immobilized halogenated carboxylic acids on the surface.⁵⁰ Additionally, a treatment with sodium hydroxide followed by dichloro(3-chloropropyl)methylsilane in toluene was used to modify some plates. The immobilized groups contained haloalkyl radicals, which are known ATRP initiators. ATRP is another common controlled radical polymerization technique, but because it relies on a transition metal catalyst, it is not usually of interest for DADMAC polymerizations. The functionalized aluminum plates were submerged in DADMAC solutions containing copper(I) chloride and bipyridine as a catalytic complex. Based off the change in contact angle and hydrophilicity of the grafted aluminum, polymerization did occur. However, the molecular weight and polydispersity of the PDADMAC chains was not characterized, and it is therefore difficult to determine if the reaction occurred through a true ATRP mechanism. A later study used immobilized monochloroacetic acid as the initiator for the grafting of PDADMAC to an aluminum surface.⁵¹ The grafted chains were then reinitiated for the polymerization of *N*-isopropylacrylamide. The resulting aluminum sheets functionalized with block copolymer chains had significantly increased wettability resulting from the hydrophilic PDADMAC and thermal responsiveness from the poly(*N*-isopropylacrylamide) blocks. Though grafting of both the homo- and block-PDADMAC polymers onto the aluminum surface was successful, the level of control achieved in these polymerizations was not fully characterized.

1.3.2 Other New Polymerization Techniques

In 1999, Martin et al. demonstrated the polymerization of DADMAC using both gamma rays and an accelerated electron beam.⁵² Both forms of ionizing radiation induced the formation of DADMAC-*co*-acrylamide copolymers using ethylene diamine tetra acetic acid as a complexing agent, sodium formate as a chain transfer agent, and sodium peroxide-sulfate as initiator in an aqueous solution. The complexing and chain transfer agents inhibited the influence of impurities and prevented unwanted cross-linking, respectively. For the systems exposed to an electron beam, higher levels of radiation (1 kGy) led to crosslinked networks. While decreasing the radiation dose or increasing the concentration of chain transfer agent could prevent

crosslinking, both were found to adversely affect the properties of the resulting polymer. Gamma irradiation led to good properties and predominately linear polymer with less dependence on radiation dosage. Because radical polymerizations are highly dependent on the type and amount of irradiation as well as the concentration of other species in solution, significant optimization was required to obtain a useful procedure. In a 2008 paper, the gamma irradiation initiated polymerization of PDADMAC was found to produce no significant crosslinking up to 70 kGy of irradiation.⁵³ At all irradiation doses above 40 kGy, 80 to 90 % conversion was reached, although increasing amounts of irradiation did not lead to higher conversion or molecular weight.

Liao et al. introduced a novel initiation system for the copolymerization of DADMAC and acrylamide in 2017 using ultrasound mediated polymerization.⁵⁴ The cavitation effect present during ultrasound initiation produces a small amount of hydrogen and hydroxyl radicals, which can increase initiation efficiency at low temperatures. Polymerization was accomplished using VA-044 as initiator, sodium benzoate as a chain transfer agent, and an aqueous urea solution as solvent in an ultrasonic cleaner at 45 KHz. Copolymer with good properties was produced after only an hour of ultrasound exposure at 30 °C. While the rapid polymerization is encouraging, as with electron beam initiation, polymerization efficiency was dependent on multiple conditions. This specific polymerization was optimized for ultrasonic time; monomer, initiator, sodium benzoate, and urea concentration; monomer ratio, temperature, and solution pH. It was reported that all variables other than sodium benzoate concentration had a distinct impact on the viability of the polymerization.

1.4 Novel Linear PDADMAC Copolymers

1.4.1 Hydrophilic Cationic Copolymers

Many of the early DADMAC copolymers included hydrophilic comonomers with no formal charge to maintain the cationic and hydrophilic properties of PDADMAC. As noted in the Wandrey review,¹⁴ the most common comonomer is acrylamide. This paper will focus on novel copolymers reported since the publication of the Wandrey review in 1999.

Vorob'eva first reported the copolymerization of DADMAC with maleic acid (Figure 1.5) in 1999.⁵⁵ When synthesized in water with potassium persulfate as initiator, the resulting random copolymers were significantly enriched in DADMAC because the ammonium monomer had a reactivity ratio nearly five times that of the acid (0.44 vs. 0.09). In the following decade, this polymerization was performed in multiple organic protic and aprotic solvents with

copolymer composition varying significantly with solvent.⁵⁶ Copolymerizations were carried out in methanol, ethanol, isopropanol, acetic acid, chloroform, and DMSO. All solvents but methanol gave random copolymers with all chains having more equal compositions than those produced in water. In acetic acid, the reactivity ratio for maleic acid (0.26) was approximately twice that of DADMAC (0.14). Copolymerization in methanol was particularly interesting because monomer feed ratio had no influence on the final polymer composition, which always remained 2:1 for DADMAC to maleic acid. It was determined that each maleic acid molecule initially complexed with two DADMAC molecules before further polymerization occurred, leading to copolymers with highly ordered structure. Since both monomer ratio and solvent had an influence on polymer composition, the copolymerization of DADMAC and maleic acid and the charge density of the resulting copolymers were particularly tunable.

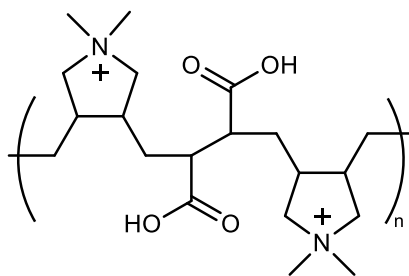


Figure 1.5 Structure of P(DADMAC-*co*-maleic acid) synthesized in methanol. Chloride counterions omitted for clarity. Adapted from ref. 56.

A copolymerization of DADMAC with *N*-vinylformamide proved interesting because of the capacity for further functionalization.⁵⁷ Copolymerizations were performed in water using a 2,2-azobisisobutyramidine dichloride with ethylenediaminetetraacetic acid dihydrochloride system as the thermally activated radical initiator. In a series of copolymerizations, the DADMAC concentration was varied from 0.13 to 1.17 M and the *N*-vinylformamide concentration was varied in accordance to maintain a total monomer concentration of 1.3 M. It was determined that the reactivity ratios were 0.13 and 1.92 for DADMAC and *N*-vinylformamide, respectively. The experimental reactivity ratios were in good agreement with previous reports for the DADMAC/acrylamide copolymerization and indicated that the final copolymer favored the incorporation of *N*-vinylformamide. A semibatch polymerization, in which *N*-vinylformamide was added in 10 portions over 10 hours, produced copolymers where more than 90 % of the DADMAC was successfully incorporated. Alkaline hydrolysis converted the *N*-vinylformamide residues to primary amines in the polymer backbone, which were then

available for further functionalization or cross-linking. The possible functionalizations examined were fluorescent labeling via coupling of dansyl chloride to the amine groups, chromophoric labeling via coupling of a dabsyl group to the amine groups, and chain extension with glycerol diglycidyl ether (Figure 1.6).

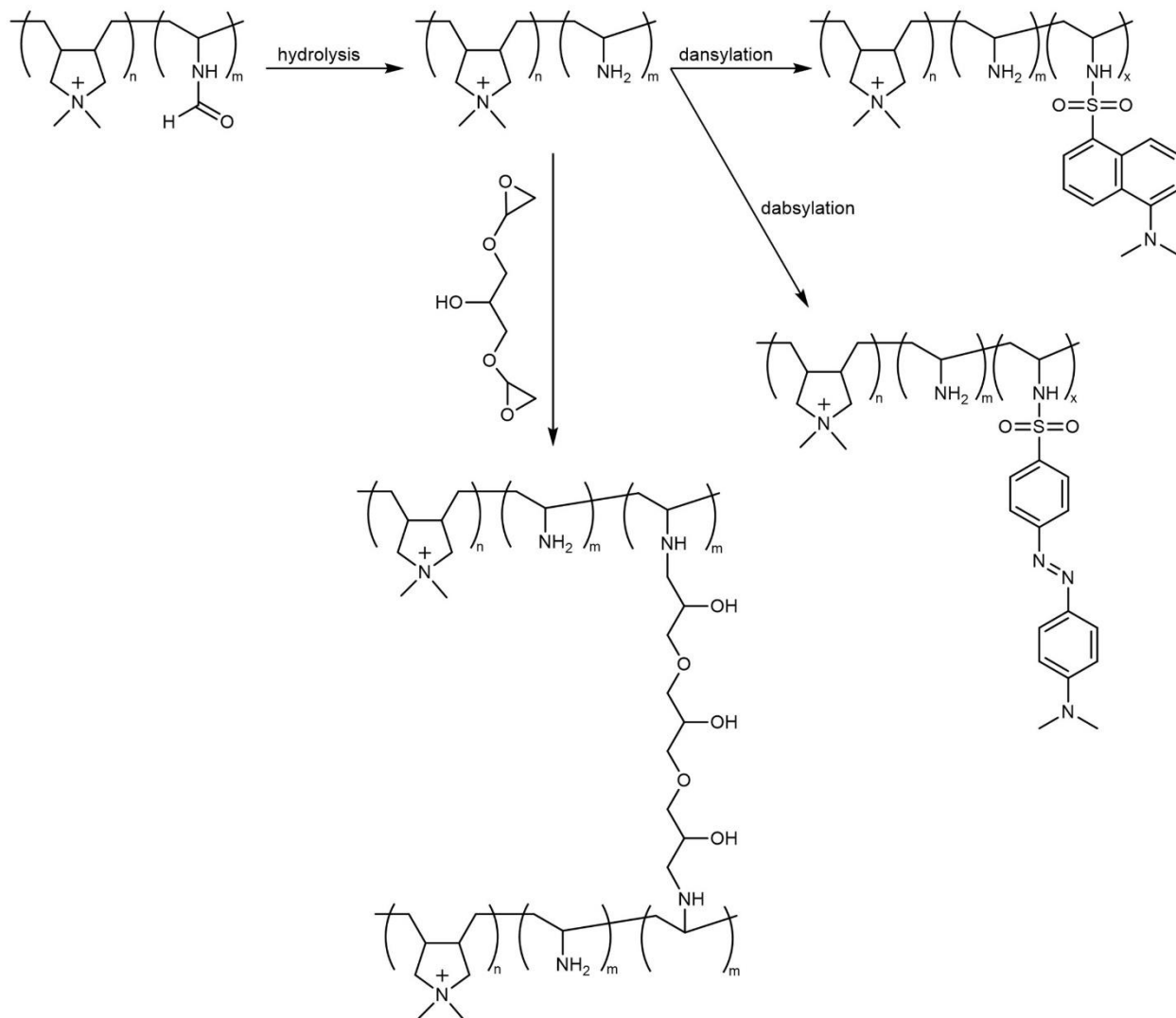


Figure 1.6 Copolymerization of DADMAC and *N*-vinylformamide followed by functionalization. Chloride counterions omitted for clarity. Adapted from ref. 57.

DADMAC copolymers with *N*-vinylformamide have also been investigated as materials for the selective removal of boron contaminants from irrigation water. Poly(styrene-*co*-divinyl benzene) microspheres were functionalized with bromoacetyl groups that allowed for the incorporation of sodium morpholine dithiocarbamate onto the microbead surface.⁵⁸ The dithiocarbamate acted as a photosensitive initiator for the oligomerization of grafted chains. The

microspheres were irradiated at 360 nm while in a solution of *N*-vinylformamide and DADMAC. However, direct grafting of the copolymer gave very low yields. The yields and grafting efficiency improved greatly when homo-poly(*N*-vinylformamide) was grafted first followed by re-initiation in the comonomer solution. The microspheres maintained their shape after the multiple grafting steps and changing the monomer ratio controlled the composition of the copolymer. Increasing the DADMAC percentage in the copolymers had a chain expanding effect and increased hydrophilicity, both of which improved the boron loading capacity of the microspheres.

Copolymerization of DADMAC with other cationic comonomers also produces cationic polymers. DADMAC has been copolymerized with a range of quaternary ammonium salts synthesized from derivatives of allyl acrylate (Figure 1.7).⁵⁹ Mathias found that DADMAC copolymers were successfully made with five of the eight tested comonomers when Irgacure 2959 was employed as the photoinitiator in aqueous solution. The copolymers derived from *tert*-butyl ester favored cross-linking and could only form soluble linear copolymers if monomer concentrations were below 30 %. For the successful polymerizations, monomer incorporation was reasonable for both species and feed ratios had a direct, though not exact, influence on final copolymer composition. The particularly notable comonomers contained piperidinium groups, which were all successfully homo and copolymerized with good efficiency.

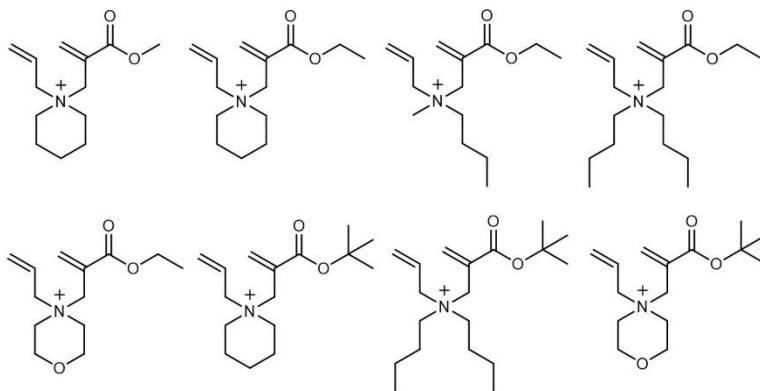


Figure 1.7 Structures of allyl acrylate derivatives copolymerized with DADMAC in ref. 59. Chloride counterions omitted for clarity.

Diallylguanidine monomers are known to undergo a similar cyclopolymerization as that of DADMAC and the resulting polymer is also used for disinfectant purposes. Copolymerization of DADMAC and diallylguanidinium acetate was successfully completed across a range of feed ratios.⁶⁰ Although the copolymers favored the incorporation of DADMAC units, final

composition was roughly tunable by changing feed ratios. The copolymerization is interesting in part because the diallylguanidinium units are more susceptible to post-polymerization modification. Copolymerizations between DADMAC and diallylguanidine as well as diallylguanidinium trifluoroacetate (Figure 1.8) were also attempted. The uncharged diallylguanidine monomer proved to be unstable at high temperatures, making it unsuitable for polymerization. The trifluoroacetate salt (Figure 1.8) could not be polymerized because labilization of the α -protons caused degradative chain transfer to monomer. DADMAC has also been copolymerized with guanidine acrylate and guanidine methacrylate.⁶¹ Copolymers were produced both in an evacuated ampule and a nitrogen purged flask and were purified through either dialysis or repeated precipitation. All procedures successfully gave water soluble copolymers, though dialysis did influence the final composition. Sivov et al. determined the reactivity ratios were an order of magnitude larger for the guanidine monomer than DADMAC in both copolymerizations. As a result, the copolymer chains were enriched in the guanidine at low conversions and incorporated some longer PDADMAC blocks at higher conversions. The final polymers obtained after longer reaction times were enriched in the guanidine monomer, but composition did vary distinctly with feed ratio. The copolymers were found to have greater thermal stability than the relevant homopolymers, possibly due to the presence of an additional type of hydrogen bond that shifts the proton toward the guanidinium moiety.

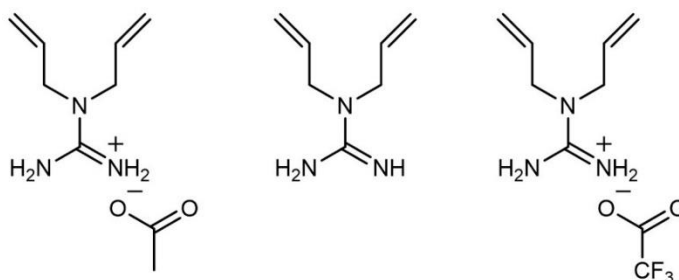


Figure 1.8 From left to right, structures of diallylguanidinium acetate, diallylguanidine, and diallylguanidinium trifluoroacetate.

1.4.2 Hydrophilic Zwitterionic Copolymers

Zwitterionic polymers and polyampholyes exhibit unique properties^{62–64} such as superhydrophilicity⁶⁵ and antifouling capacity.⁶⁶ To access these properties, DADMAC can be copolymerized with either anionic or zwitterionic comonomers. In a 1999 study, DADMAC was copolymerized with the zwitterionic 3-(*N,N*-diallyl-*N*-methyllummonio)propanesulfonate (Figure

1.9).²⁶ The photopolymerization was carried out in a Rayonet photoreactor under 300 nm light using 2-hydroxy-1-[4-(hydroxyethoxy)phenyl]-2-methyl-1-propanone (Irgacure 2959) as initiator. The polymerizable moieties, and therefore reaction ratios, of the two monomers in this copolymerization are very similar, so the final copolymer composition to feed ratio relationship was highly linear. The combination of ionic charge and dipole character in the copolymer meant the chain conformation in solution was closely related to composition and solvent polarity, which provided for tunable solution viscosities and microphase separation. Another sulfonate moiety was copolymerized with DADMAC in the form of 2-acrylamido-2-methyl propane sulfonic acid (Figure 1.9).⁶⁷ The copolymer was grafted from locust bean gum using *N,N*-methylene-bisacrylamide as a cross-linking agent in the presence of bentonite to produce a network of zwitterionic polymer.

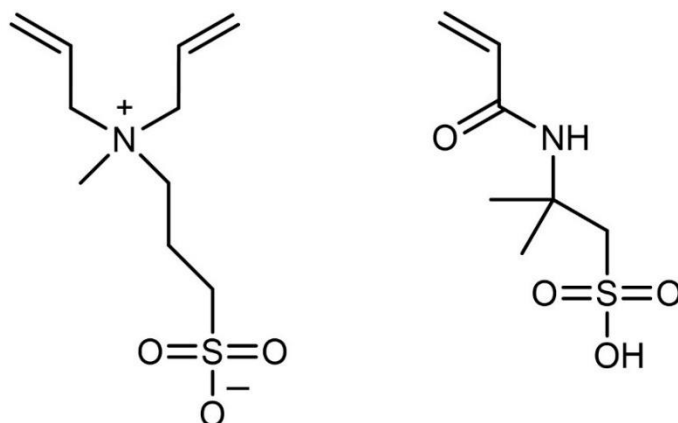


Figure 1.9 Structures of DAMAPS (left) and 2-acrylamido-2-methyl propane sulfonic acid (right).

In a 2016 study, porous polyethylene sheets were submerged in an aqueous solution of DADMAC and vinyl sulfonic acid sodium salt.⁶⁸ The outer surface of the membranes were grafted with zwitterionic chains, but the polyethylene pores were too small to support grafting. After the functionalized membranes were submerged in an ethanol solution for two days, sodium chloride precipitated. The salt precipitation indicates that the cationic and anionic comonomer units were also serving as counterions via either interchain or intrachain interactions. The influence of interchain interactions is particularly interesting in the case of spiroxazine-diallylamine/DADMAC copolymers, as they are only zwitterionic when exposed to UV irradiation (Figure 1.10).⁶⁹ Diallylamine hydrochloride was copolymerized with DADMAC in a 10:1 molar ratio via a radical polymerization using ammonium peroxydisulfate as initiator. The

amine monomer units were then functionalized with a photochromic spiroxazine unit. Though the final copolymer composition was not characterized, the final polymer had good photochromic character, demonstrating a color change upon UV exposure. The properties of DADMAC copolymers were directly related to the present electrostatic forces, which could be seen in copolymers that can easily and reversibly be converted between a cationic and zwitterionic form.

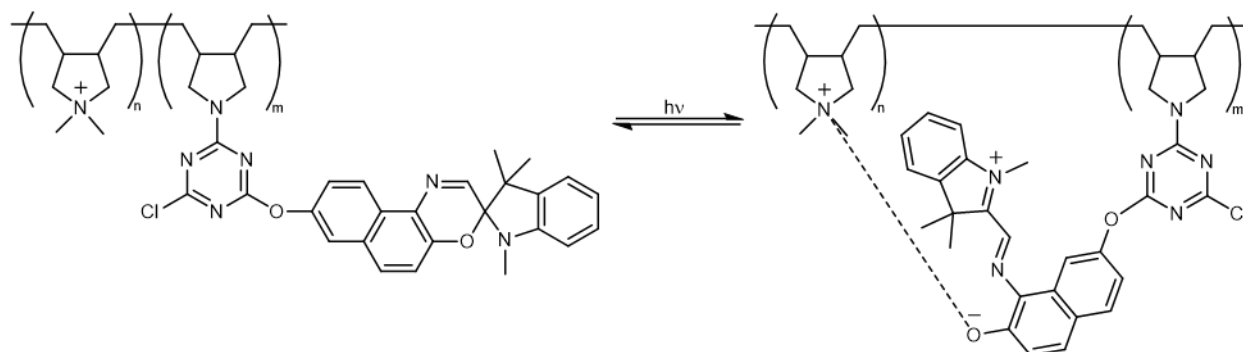


Figure 1.10 The structures of spiroxazine-diallylamine/DADMAC copolymers without (left) and with (right) UV irradiation. Adapted from ref. 69.

1.4.3 Hydrophobic and Amphiphilic Copolymers

Ionic character is an important part of hydrogels as it directly influences swelling and phase transitions. In one study,⁷⁰ a small amount of DADMAC (0.03 or 0.05 mol fraction) was copolymerized with 1-vinyl-2-pyrrolidone and *N*-vinylcaprolactam using 1-1'-divinyl-3,3'-(ethane-1,1-diy)]di(1-vinyl-2-pyrrolidone) as a cross-linker. Charged polymer networks with notably different properties from their uncharged counterparts were synthesized in a water/ethanol mixture using gamma radiation for initiation. As would be expected, since PDADMAC is a linear cyclopolymer, the DADMAC units were incorporated into the linear portions of the copolymer backbone instead of acting as cross-linkers. As a result, swelling and phase transition properties did not change significantly with the increase in DADMAC concentration. However, the inclusion of DADMAC produced a first-order phase transition, where increasing nonsolvent concentration caused network collapse and a decrease in gel volume.

The efficacy of PDADMAC as a flocculant in the treatment of contaminated water can be improved through copolymerization. Copolymers with acrylamide tend to achieve higher molecular weight and better material properties, but the incorporation of hydrophobic comonomers can also improve flocculation efficiency. A series of novel tri-copolymers

containing DADMAC, acrylamide, and vinyl trimethoxysilane (Figure 1.11) were synthesized in 2002.⁷¹ Concentrations of the silane were kept at either 0.5 or 1.0 mole percent as higher concentrations led to insolubility in water. It was found that the amphiphilic polymers had superior flocculation and decoloration properties though more mass of the polymer was needed because of the lower charge density.

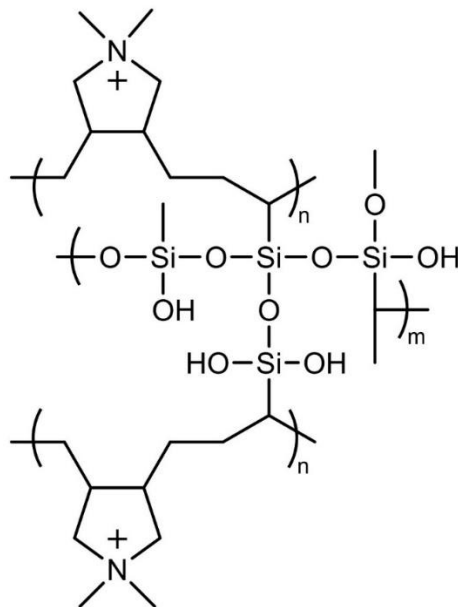


Figure 1.11 DADMAC copolymers with trimethoxysilane. Chloride counterions omitted for clarity. Adapted from ref. 71.

The copolymerization of DADMAC and sulfur dioxide to make aliphatic polysulfones was first reported in 1966⁷² and has since been expanded upon greatly due to the beneficial material properties of polysulfones. By themselves, the copolymers are hydrophilic, but adding a small amount of a hydrophobic monomer can produce useful intermolecular associations. To produce hydrophobic monomers with increased organic character, one methyl group of DADMAC was replaced with an octadecyl alkyl chain.⁷³ Reacting equivalents of sulfur dioxide with diallyl monomers, a small percentage of which were in the hydrophobic octadecyl form, produced terpolymers (Figure 12). As would be expected, the higher concentrations (up to 7.5 %) of hydrophobic monomer led to polymers with lower water solubility. Increasing hydrophobicity from 0 to 5 % also dramatically increased the viscosity of the solution. At 7.5 %, the viscosity dramatically decreased, which was theorized to be a result of favorable intramolecular interactions overwhelming those between chains.

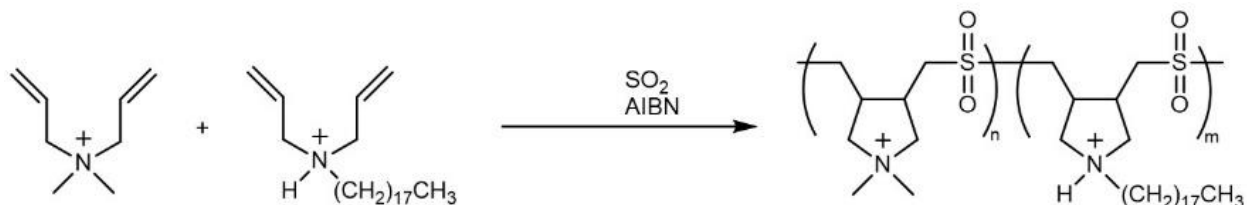


Figure 1.12 Amphiphilic terpolymers of DADMAC, sulfur dioxide, and diallylmethyloctadecylammonium chloride. Chloride counterions omitted for clarity. Adapted from ref. 73.

Cross-linking is one way to produce water-insoluble polymer networks out of DADMAC monomers. PDADMAC can be cross-linked without the addition of a cross-linking agent, since PDADMAC chains inherently contain some unreacted double bonds resulting from a small percentage of monomer units that did not cyclopolymerize. However, the amount and distribution of the non-cyclic units can be difficult to control, and significant amounts of cross-linking are not normally seen in homo-PDADMAC. Copolymerization with a small amount (2%) of hydrophobic divinylbenzene led to PDADMAC copolymer networks that were insoluble in water.⁷⁴ The slight hydrophobicity resulting from the benzyl groups meant the polymer swelled most in solvents like tetrahydrofuran and diethyl ether and relatively less in water or methanol. Due to this unique behavior, the networks could be used as matrices for phase transfer catalysts, which was a direct result of the amphiphilic nature of the polymer.

Copolymerizing DADMAC with a high percentage of a very hydrophobic monomer produces entirely hydrophobic polymers. Chlorotrifluoroethylene (CTFE) is a common chlorofluorocarbon monomer used to form polymers with high stability and insolubility in both water and organic solvents. CTFE was shown to be copolymerizable with DADMAC in a variety of solvents using *tert*-butylperoxypivalate or di-*tert*-butyl peroxide as initiator.⁷⁵ Pentafluorobutane with a fluorocarbon surfactant was found to be the most effective solvent system, giving an 85% yield. Additionally, elevated temperatures favored better conversion and monomer incorporation. All the reactions produced copolymers with reasonable incorporation of both monomers, but the ratio was difficult to control and the DADMAC monomer was added favorably. For higher concentrations of CTFE, the polymers were found to be insoluble in both water and common non-fluorinated organic solvents. While the solubility was indicative of successful copolymerization, it made the polymers difficult to process or thoroughly characterize.

Another interesting characteristic of hydrophobic DADMAC copolymers is their ability to form latex particles in a surfactant free solution, which expands the usefulness of PDADMAC in the textile industry as a binder for fabric dye. Li, Zhu, Sunintaboon, and Harris sought to graft polymer chains to a PDADMAC backbone to form particles with a hydrophobic core and charged shell. Their 2003 work attempted to form redox pairs between the ammonium groups in commercially available PDADMAC and *tert*-butyl hydroperoxide, which should produce nitrogen radicals that can serve as initiation sites for grafting.⁷⁶ When PDADMAC was exposed to *tert*-butyl hydroperoxide followed by methyl methacrylate, only 12 % of the ammonium groups were converted to radicals and no quantifiable grafting was observed, indicating this process is not suitable for quaternary ammonium polymers. However, the copolymerization of DADMAC with methyl methacrylate and *N*-butyl acrylate in water using potassium persulfate as initiator led to the formation of stable, cationic latex particles (Figure 1.13).⁷⁷ Cross-linking through the addition of water-soluble hydroxyethyl acrylate greatly improved copolymer properties. FT-IR characterization of the polymers indicated the incorporation of ester groups and the disappearance of carbon-carbon double bonds. However, the final copolymer composition was not quantitatively determined making it difficult to determine the effectiveness of monomer incorporation.

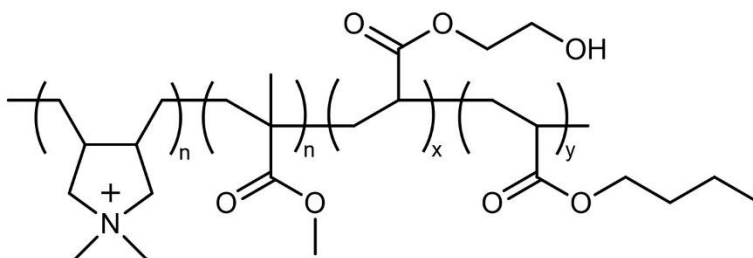


Figure 1.13 Structure of the latex particles formed from copolymers of DADMAC, methyl methacrylate, hydroxyethyl acrylate, and *N*-butyl acrylate. Chloride counterions omitted for clarity Adapted from ref. 76.

1.5 Diallyldimethylammonium with Other Counterions

As mentioned in the introduction, the first example of cyclopolymerization used DADMABr as the monomer rather than DADMAC.⁴ In 1958, the Butler group once again turned to PDADMABr, which was synthesized from the bromine form of the monomer using *tert*-butyl hydroperoxide, for degradation studies to help elucidate the structure of the polymer.⁸ Though DADMAC is the most common form of the monomer, non-chloride counterions are also used as a way to change polymer properties.

In 1983, Mastragostino and Valcher used PDADMABr as a bromine complexing polymer in a zinc-bromine battery.⁷⁸ Commercial PDADMAC was added to a sodium bromide solution to produce the polymer. Like PDADMAC, PDADMABr has been synthesized as gels in aqueous solution using a crosslinker. Philippova and Starodoubtzev reacted DADMABr with a small amount of *N,N'*-methylenebisacrylamide in aqueous solution to form swollen gels in which to study the diffusion of pyrene.⁷⁹ It was shown that systems with a crosslinker concentration below 0.80 wt. % did not produce polymer networks and maintained water solubility.⁸⁰ PDADMABr has also been used as a polyelectrolyte film in the layer-by-layer deposition of magnetite nanoparticles⁸¹ and silver halide microcrystals⁸² and as a polymer matrix for the formation of thin films containing guest-host-type complexes of dye molecules and sulfonated calixarenes.⁸³

While PDADMAC and PDADMABr are often synthesized from the commercially available monomers, the incorporation of other anions relies on ion exchange at either the polymer or monomer level. In 2003, Brylev and coworkers exchanged the chloride ion in commercially available DADMAC to bromide, fluoride, and iodide as well as the polyatomic ions tetrafluoroborate (BF_4^-) and bistriflimide (TFSI^-).⁸⁴ The monomers were then reacted with pendent double bonds in a poly(ethylene glycol-*co*-3-chloro-2-chloromethyl-1-propene) to create a cross-linked matrix (Figure 1.14). The anion identity did not significantly influence the cross-linking ability but polymers containing larger, less nucleophilic (i.e., TFSI^-) counterions were more conductive.

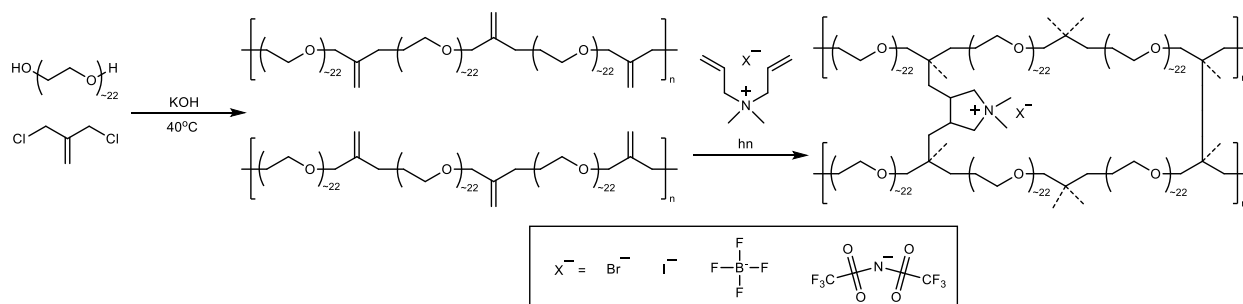


Figure 1.14 Poly(ethylene glycol-*co*-3-chloro-2-chloromethyl-1-propene) copolymer cross-linked with the addition of DADMA units. Adapted from ref. 84.

In 2010, the Mecerreyes group also began to explore the influence of a variety of counterions on the polymerization and properties of DADMA monomers.⁸⁵ DADMAC in aqueous solution was added to stirring aqueous solutions of LiTFSI , potassium hexafluorophosphate (KPF_6), NaBF_4 , and potassium thiocyanate (KSCN). The resulting monomer salts were either insoluble in water (TFSI^- and PF_6^-) or only somewhat soluble in water

(SCN⁻ and BF₄⁻). The monomers with different counterions were then polymerized either alone or together in the bulk using AIBN as initiator. In a further study, the group compared the ion exchange of the DADMAC monomer followed by polymerization to the ion exchange of commercially available PDADMAC.⁸⁶ Both pathways produced polymers with the desired anions, but ion exchange after polymerization was the only method reported to produce polymers with film forming properties. Post-synthetic ion exchange was also used to produce poly(ionic liquid)s and films of PDADMA with dicyanamide (N(CN)₂⁻) and tricyanomethanide (C(CN)₃⁻) counterions for use in CO₂ separation.⁸⁷ A partial anion exchange produced “copolymers” containing 1.25 to 10 % DADMA(TFSI) units and the remainder DADMAC, which functioned as amphiphilic flocculants for water purification.⁸⁸ Homopolymers comprised entirely of DADMA(TFSI) were charged with the ionic liquid 1-ethyl-3-methylimidazolium dicyanamide to produce conductive poly(ionic liquid) iongels for potential use in batteries.⁸⁹ The Mecerreyes group also demonstrated that the controlled-radical polymerization method of Polymerization-Induced Self Assembly (PISA) could be used to synthesize PDADMA(TFSI).⁴⁸ As discussed previously, controlled radical polymerization of DADMAC has not been thoroughly proven. This work indicates that the PISA method successfully controlled the end groups of the DADMA(TFSI) blocks but not their molecular weight. Since the blocks were successfully functionalized at either one or both ends with a thiocarbonylthio group, they could be used to initiate the polymerization of polystyrene to form PDADMA(TFSI)-*b*-PS di- and tri-block copolymers.

Converting the chloride counterion to hydroxide (OH⁻) maintains water solubility of the monomer and polymer while expanding usable polymerization conditions. Copolymerization of maleamic acid and DADMAC resulted in the formation of pH-controlled polyampholytes (Figure 1.15).⁹⁰ However, the polymerization of maleamic acid was carried out in alkaline media (pH>8). Multiple studies have copolymerized maleamic acid with DADMA(OH⁻) rather than DADMAC to preempt the less-controlled ion exchange that would occur during polymerization in basic solution.⁹⁰⁻⁹² Films submerged in potassium hydroxide solution⁴⁷ or successively titrated by silver sulfate and barium hydroxide⁹³ underwent post-polymerization ion exchange to hydroxide. In 2018, Jung and Weichold used an ion exchange resin column to produce DADMA(OH) which was copolymerized with methacrylamide to produce statistical copolymers with good OH⁻ transport capabilities.⁹⁴

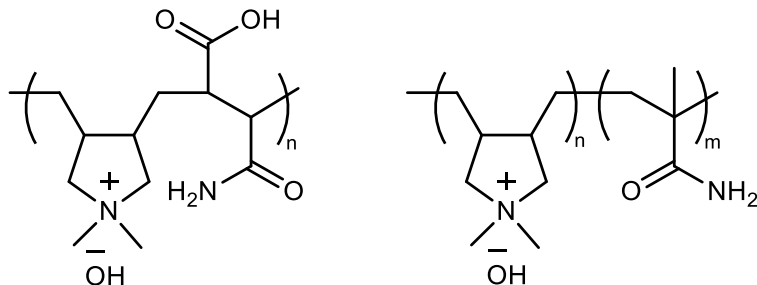


Figure 1.15 Structures of copolymer of DADMA(OH) with maleamic acid (left) and methacrylamide (right). Adapted from refs. 90 and 94.

1.6 Other Cationic Nitrogen Diallyl Monomers

1.6.1 Polymerization of Diallylguanidinium Monomers

As with diallylammonium monomers, diallyl guanidine monomers undergo cyclopolymerization to produce five membered rings containing cationic nitrogen¹⁰ and exhibit biocidal activity at some pH.⁹⁵ Guanidinium monomer with positive charge at all pH values was produced by substituting the protons of the diallyl guanidine with alkyl groups. This section will focus on the polymerization of the formally cationic guanidinium chloride, which demonstrates significant structural similarity to DADMAC.

2,2-Diallyl-1,1,3,3-tetraethylguanidinium chloride (AGC) was first polymerized by radical copolymerization with *N*-vinylpyrrolidone in DMSO using AIBN as the initiator (Figure 1.16).⁹⁶ It was found that reactivity ratios of the two monomers were within the same order of magnitude with the AGC reactivity ratio being somewhat higher. In addition, a greater ratio of AGC in the feed was reported to lower polymerization rate overall. Gorbunova used a similar free radical system to copolymerize AGC with *N*-phenylmaleimide, *N-p*-carboxyphenylmaleimide,⁹⁷ and *N*-acetoxyphenylmaleimide (Figure 16).⁹⁸ The copolymerizations with imide monomers demonstrated low levels of change in copolymer ratios despite large changes in monomer feed ratios. UV analysis of the comonomer solutions indicated that the AGC and maleimides behave as electron donors and acceptors respectively, leading to interactions between the species that promoted alternating copolymers. The same behavior was observed in the copolymerization of AGC and maleic acid (Figure 16).⁹⁹ The reactivity ratio of AGC was reported to be two to ten times greater than that of maleic acid in chloroform, methanol, and ethanol but approximately five times less in the bulk. Copolymerizations of AGC and 2-hydroxyethylacrylate (Figure 16) were also carried out in bulk and methanol to produce copolymers with alternating behavior.¹⁰⁰ The chloride ions of the AGC units were then

exchanged with hydroxide and a number of biologically active acids in the anionic form to produce biocidal materials.

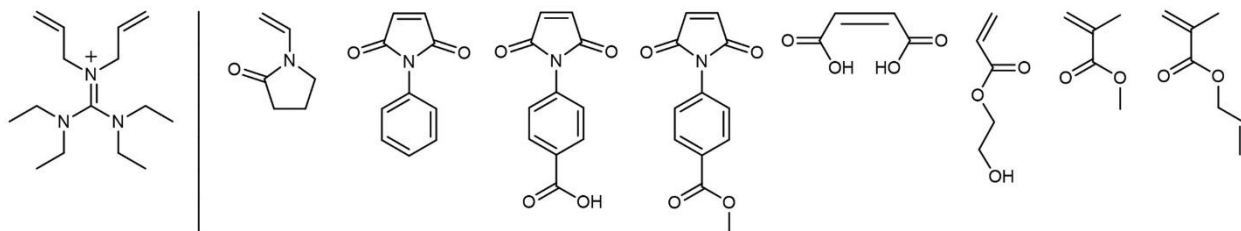


Figure 1.16 Structures of AGC and studied comonomers.

AGC has also been copolymerized with water insoluble monomers to produce amphiphilic copolymers. Unlike copolymerizations with maleimides or maleic anhydride, the copolymerization of AGC with methyl methacrylate (Figure 1.16) did not exhibit alternating behavior.¹⁰¹ In the bulk, copolymers were enriched with methyl methacrylate units, but polymerization in methanol led to enrichment in AGC. The opposite trend was observed during copolymerization with allyl methacrylate (Figure 1.16). Since both AGC and allyl methacrylate undergo cyclopolymerization, the resulting copolymers were comprised of both five and six membered rings.

1.6.2 Polymerization of Cyclic Diallylammonium Monomers

The first report of the synthesis and polymerization of cyclic diallylammonium monomers in 1967 included both diallylpiperidinium and diallylmorpholinium chloride.¹² The objective was to extend cyclopolymerization to monomers containing cyclic units and to increase the degree of polymerization in comparison to that reported for PDADMAC. The polymerization of diallylpiperidinium chloride was carried out for 24 hours, at 30 °C, in DMSO with 34.1 wt. % monomer and either 1 or 2 wt. % ammonium persulfate as initiator. The temperature, solvent, and initiator identity were the same for the polymerization of the morpholinium monomer, but the monomer concentration was 17 wt. % and initiator concentrations of 1, 2, and 3 wt. % were tested. All polymerizations resulted in conversions between 58 and 98 % and intrinsic viscosities between 0.23 and 0.57. As is expected for radical polymerizations, increasing initiator concentrations led to an increase in conversion but decrease in measured intrinsic viscosity, which indicated that cyclopolymerization was suitable for preparing spirocyclic polymers containing cationic nitrogen groups. In 1997, De Vynck and Goethals reported the first synthesis of a diallylpyrrolidinium bromide monomer and its radical cyclopolymerization.¹⁰² The

spirocyclic polymer was synthesized using AIBN as an initiator in a methanol/acetonitrile solvent system and ammonium persulfate as an initiator in water. Both methods yielded polymer with the best properties at high monomer and initiator concentrations, but neither returned chains of high molecular weight. A 2002 study used the same polymerization procedure to make polymers of high enough molecular weight to be used as polyelectrolyte films in a layer-by-layer clay assembly.¹⁰³

Functionalized versions of the cyclic monomers are also polymerizable. 4-Methoxycarbonyl-1,1-diallylpiperidinium chloride was polymerized in DMSO using AIBN.¹⁰⁴ The methoxy functionalized monomer was also reacted with dialyloctadecylammonium chloride and sulfur dioxide to form a terpolymer (Figure 1.17). Acidic hydrolysis of the terpolymer followed by exposure to base produced a pH responsive, water-soluble polyzwitterion, with interesting surfactant interactions. *N,N*-diallyl morpholinium bromide and *N,N*-diallylpiperidinium bromide monomers were copolymerized with acrylamide via microwave irradiated free radical polymerization.¹⁰⁵ With the addition of a cross-linker, the resulting hydrogels demonstrated good metal adsorption capabilities. Hydrogels were also produced from the copolymerization of *N,N*-diallylpyrrolidinium bromide with *N*-isopropylacrylamide and acrylic acid.¹⁰⁶ The emulsion polymerization was carried out in a continuous phase of (2-hydroxyethyl sulfosuccinate) sodium salt using AIBN as initiator and ethylene glycol dimethacrylate as a cross-linking agent. Increasing the ratio of *N,N*-diallylpyrrolidinium in the feed increased the hydrophilicity of the amphoteric hydrogel.

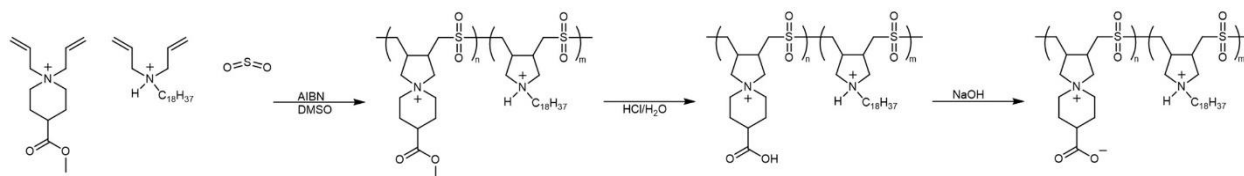


Figure 1.17 Synthesis of terpolymers from dialyloctadecylammonium chloride, methoxycarbonyl-1,1-diallylpiperidinium chloride, and sulfur dioxide. Chloride counterions omitted for clarity. Adapted from ref. 104.

One of the unique properties of PDADMAC is its high alkaline stability. Similar polymers synthesized from cyclic monomers double down on this characteristic because the spirocyclic ammonium is even more hindered to nucleophilic attack.¹⁰⁷ A 2017 study by Olsson, Pham, and Jannasch examined the alkaline stability of polydiallylammoniums produced from monomers with a variety of ring structures and chemistries (Figure 1.18).¹⁰⁸ Ammonium

persulfate in aqueous monomer solution was used to produce homopolymers containing five, six, and seven-membered ammonium rings and a morpholinium ring. The polymers were dissolved in potassium deuteroxide and exposed to heat then examined by NMR spectroscopy to characterize the changes in structure resulting from decay. It was determined that the seven-membered oxygen containing rings were the least stable while the six-membered ring was the most stable. The stability of polydiallylpiperidinium makes it useful as an anion exchange membrane for use in fuel cells applications requiring high hydroxide concentrations.

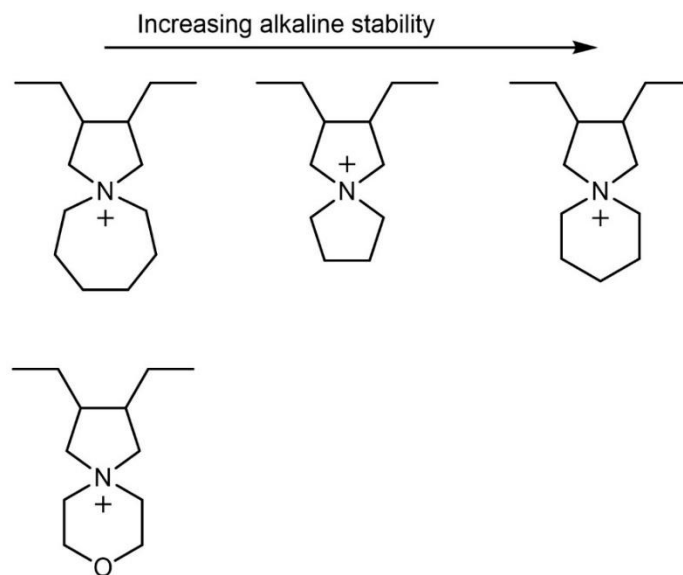


Figure 1.18 Structures of the spirocyclic repeat units studied in ref. 108. Chloride counterions omitted for clarity.

In 2017, Strasser, Graziano, and Knauss synthesized block polysulfones containing poly(diallylpiperidinium hydroxide) blocks.¹⁰⁹ A photosensitive iniferter was used to make cationic oligomers difunctionalized with (4-fluorophenyl)sulfide groups. The use of an iniferter ensured control over the polymerization allowing for quantitative end capping without having to use controlled radical polymerization. After oxidation of the sulfides to sulfones and ion exchange from chloride to hexafluorophosphate, the oligomers were reacted with bisphenol-A and (4-fluorophenyl)sulfone to produce block copolymers (Figure 1.19). This polymerization technique was unique in its ability to produce copolymers from a combination of radical and condensation polymerization steps. As expected, the cationic block polysulfones exhibited excellent alkaline stability. Diallylpiperidinium bromide has also been copolymerized with styrene and acrylonitrile in divinylbenzene and benzoin ethyl ether.¹¹⁰ When a glass mold was

filled with the monomer solution and exposed to UV irradiation cross-linked membranes with good flexibility, transparency, alkaline stability, and ion conductivity were produced.

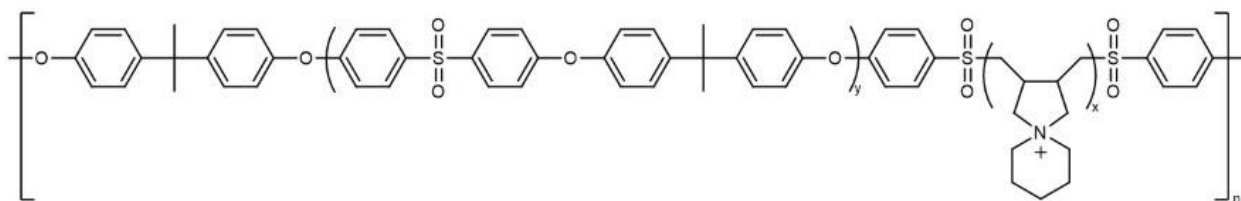


Figure 1.19 Structure of polydiallylpiperidinium/polysulfone block copolymers. Counterion omitted for clarity. Adapted from ref. 109.

1.7 Conclusions and Outlook

Since the discovery of its cyclopolymerization in the 1950s, DADMAC and its copolymers have gained widespread interest and usage. Due to its particularly high charge density, good chemical stability, reasonable cost and availability, and low toxicity, PDADMAC is a useful material for a wide variety of applications. While initially developed for use in specialty paper processing, the polyelectrolyte has become common in everything from cosmetics to water treatment. The incorporation of DADMAC into copolymers, which have a larger range of possible material properties, has further expanded its usefulness. In 1999, Wandrey, Hernandez-Barajas, and Hunkeler summarized much of the early work in understanding the synthesis, kinetics, properties, characterization, and applications of DADMAC polymers. Since this review, the use of DADMAC and similar monomers has continued to be an area of interest. Examining the literature that was either outside of the scope of the Wandrey review or has been published since 1999 demonstrates that the synthesis of novel diallylammonium polymers is an area of active progress.

Though PDADMAC has traditionally been prepared through free radical polymerization, the growing interest in controlled/living radical polymerization has extended to DADMAC. Multiple RAFT polymerization systems have been attempted with varying levels of success. While some studies reported decreased molecular weight distribution at low conversion or termination with functionalized end-cappers, true control has not proven readily reproducible. The controlled polymerization of DADMAC will likely be an area of continued research. Other novel methods for the generation of radicals in solution, such as gamma ray exposure and ultrasonication, have also been shown to initiate the polymerization of DADMAC.

Several novel copolymers have been synthesized to expand upon the properties inherent to DADMAC in the past two decades. Copolymerization with nonionic hydrophilic monomers like maleic acid and *N*-vinylformamide retain the water solubility of the final polymer but allow for tunability of the charge density based on solvent and monomer feed ratio. Syntheses using comonomers that also contain ammonium and allyl moieties are particularly controllable due to the similar chemistries and reactivity ratios of the monomers. When copolymers incorporated DADMAC and monomers with either a permanent or induced formal charge, electrostatic interchain interactions led to interesting chain conformation and behavior. Many synthetic routes have been explored for the preparation of DADMAC containing copolymers with less hydrophilic character. The addition of a small amount of the ammonium monomer to an otherwise hydrophobic polymer can produce chains that are water stable but demonstrate unique interchain interactions between the ionic and nonionic groups. Conversely, the incorporation of a hydrophobic comonomer into PDADMAC can improve the polymer properties by decreasing the intrachain repulsion between the charged groups.

Though DADMAC is the most common and widely applied form of the monomer, other counterions can be incorporated during monomer synthesis or by ion exchange of either the monomer or polymer. Exchange from chloride to other halides or hydroxide maintains high water solubility while allowing for different electronic properties. Monomers and polymers with polyatomic counterions demonstrate changes in solubility, with some even being insoluble in water. The synthetic techniques used to make PDADMAC can also be expanded to other diallylammonium monomers, which have comparable but unique properties. Diallylguanidinium monomers have been copolymerized with *N*-vinylpyrrolidone, maleimides, maleic acid, 2-hydroxyethylacrylate, and methyl methacrylate. If the two methyl units on DADMAC are replaced by a single ring, the resulting polymer has a spirocyclic structure. The inclusion of rings, whether five, six, or seven membered, increases the steric hindrance against nucleophilic attack, which makes the polymers even more base stable.

DADMAC and similar monomers have been incorporated into a large variety of polymers, which take advantage of many synthetic techniques. The resulting materials demonstrate a range of properties while maintaining the inherent benefits of cyclopolymerized ammonium monomers. Due to the availability and low cost of DADMAC, it is likely to be of continued interest as a monomer in novel polymer systems. Hydrophobic and amphiphilic

copolymers may draw the most attention moving forward since they offer the greatest potential for novel properties and applications. In addition, the synthesis of spirocyclic ammonium polymers may be an area of robust research because of their particularly high alkaline stability, which could be further explored.

1.8 Context of the Work in This Thesis

By their nature, cationic materials are likely to be hydrophilic, so the production of insoluble polymer materials containing cationic functionality can prove difficult. As a result, there are far fewer examples of water insoluble polymers containing diallyldimethylammonium units than water soluble polymers. While the hydrophobic nature of DADMAC and polymers thereof is a valuable property for many applications, it is also inherently limiting. Many modern applications of polymers rely on materials that are insoluble in their environment. In particular, there is need for new advanced membrane materials with good physical properties and longevity. The work presented in this thesis seeks to overcome this gap in the diallylammonium polymer literature by developing multiple procedures for the synthesis of copolymers containing both diallyldimethylammonium repeat units and hydrophobic repeat units.

Because few linear, water insoluble DADMAC copolymers exist in the literature, a wide variety of hydrophobic components could be of interest. To narrow our focus, we chose to target copolymer materials hypothesized to form polymeric membranes with good properties. The desire was to produce copolymer materials that married the beneficial properties of PDADMAC, like conductivity, useful electrostatic interactions, and counterion exchange capacity, with the properties of certain hydrophobic polymers, like flexibility, strength, and stability. In addition, we chose to focus on hydrophobic polymers that are already employed industrially to improve the commercial viability of the synthesized copolymers.

A notable discovery presented in the literature contained within Section 1.6 is the facile nature of the counterion exchange from the chloride counterion to other counterions. While the counterion exchange has been completed with a variety of halide and polyatomic counterions, hexafluorophosphate was of the most interest for our work because DADMA(PF₆) is insoluble in water and soluble in polar, aprotic, organic solvents. The unique solubility of the PF₆ monomer and polymer salts facilitate the copolymerization with hydrophobic comonomers by increasing the available cosolvents.

The overarching purpose of this work was to develop novel methods to produce water insoluble copolymers with membrane forming capacity containing diallyldimethylammonium units. Two main hypotheses were tested:

Hypothesis 1: Copolymers with reasonable film-forming capacity can be synthesized through the radically initiated copolymerization between DADMA(PF₆) and commercially available, hydrophobic vinyl monomers. Hypothesis 1 was tested by the copolymerization between methyl methacrylate and DADMA(PF₆) presented in Chapter 2.

Hypothesis 2: An iniferter-based synthesis can produce multiblock copolymers containing PDADMA(PF₆) blocks and high-performance polymer blocks with reasonable film-forming capacity. Hypothesis 2 was tested through the synthesis of multiblock polysulfones in Chapter 3 and the synthesis of multiblock polyaramides and polyimides in Chapter 4.

A discussion of the results as they support both hypotheses, and the implications of this information can be found in Chapter 5.

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CHAPTER 2

SYNTHESIS AND CHARACTERIZATION OF COPOLYMERS FROM DIALLYLDIMETHYLAMMONIUM HEXAFLUOROPHOSPHATE AND METHYL METHACRYLATE

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2.1 Abstract

This work presents the bulk copolymerization of diallyldimethylammonium hexafluorophosphate (DADMA(PF₆)) and methyl methacrylate (MMA). The ion exchange of DADMAC from chloride to hexafluorophosphate yielded a water insoluble form of the ammonium monomer that is soluble in MMA. Copolymerization was successfully carried out over a wide range of monomer feed ratios, which correlated strongly to the composition of the final copolymer. The highly tunable nature of the copolymerization made it possible to incorporate large percentages of either monomer. Studies of copolymer composition at a range of reaction times indicated the incorporation of MMA was slightly favored over that of DADMA(PF₆). While all copolymers formed water-stable standalone films, those with high incorporations of MMA had additional strength, flexibility, and clarity. The facile, reproducible polymerization method developed herein produced copolymers containing diallyldimethylammonium moieties that can be processed into hydrophobic polymer films.

2.2 Introduction

Cationic polyelectrolytes are an increasingly important class of materials due to their purification capabilities,^{1,2} biocidal activity,^{3,4} and electrochemical properties.^{5,6} Of the possible cationic moieties, quaternary ammonium polymers are the most versatile and widely used.^{7,8} Some of the first and most relevant cationic polyelectrolytes were developed through the polymerization of diallyldimethylammonium chloride (DADMAC), which was first carried out by Butler and coworkers in the 1950s.^{9,10} The polymerization of DADMAC occurs through a unique cyclopolymerization mechanism to produce linear homopolymer comprised of

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intramolecularly cyclized monomer.^{11,12} Due to the hydrophilic, permanently charged ammonium groups, PDADMAC has high water solubility and demonstrates strong polyelectrolyte properties in solution.^{8,13-16} DADMAC and its resulting polymer are inexpensive, easily synthesized, and nontoxic.¹⁷ Additionally, the electron poor nitrogen of the PDADMAC repeat unit is hindered to nucleophilic attack due to its cyclic structure, making PDADMAC more base stable than polycations with pendant quaternary ammonium groups.¹⁸ The most important historical and modern use of PDADMAC is as a flocculant in the treatment of contaminated water.¹⁷ It is also industrially significant as an additive in paper and textile manufacturing,¹⁹⁻²² antimicrobial materials,²³⁻²⁵ and cosmetics.²⁶⁻²⁸

New structures and materials have been produced through the copolymerization of DADMAC with a variety of comonomers. Copolymerization of DADMAC with both charged and uncharged, water-soluble monomers are widely reported in the literature. The first and most common comonomer investigated has been acrylamide, which is used mainly to overcome the often limited molecular weight of homo-PDADMAC.²⁹⁻³¹ However, in a free-radical copolymerization, the reactivity ratio of acrylamide is significantly higher than that of DADMAC,³² making it difficult to tune polymer composition or charge density. Copolymerization with *N*-methyl-*N*-vinylacetamide is nearly ideal³³ while the reactivity ratios in the copolymerization with maleic acid vary largely with solvent.³⁴ Cyclocopolymerization with other cationic diallyl monomers like allyl acrylate quaternary ammonium salts³⁵ or diallylguanidinium acetate³⁶ maintains the high charge density of the polymer while increasing its organic character or thermal stability. Zwitterionic copolymers, which exhibit superhydrophilicity and antifouling capacity,³⁷ have been synthesized through the copolymerization of DADMAC with anionic and zwitterionic monomers such as acrylic acid³⁸ and 3-(*N,N*-diallyl-*N*-methylammonio)propanesulfonate.¹³ The copolymerization of DADMAC has produced polymers with a range of unique structures and properties and has largely expanded the possible uses of DADMAC-containing materials beyond those of the homopolymer.

Because of the high water and low organic solubility of DADMAC, copolymerization with hydrophobic monomers is quite challenging.³⁹ The copolymerization of DADMAC with acrylonitrile in a highly acidic solution has been reported, but the desired incorporation of ammonium groups was very low and no quantitative analysis of composition was performed.⁴⁰ Nanoparticles were produced through the copolymerization between styrene and ammonium

monomers, but unlike the other ammonium monomers, the nanoparticles synthesized with DADMAC have properties indicating they are effectively homo-polystyrene.⁴¹ The copolymerization of DADMAC with the water-insoluble comonomer vinyl acetate is unique because the reactivity ratio of DADMAC was reported to be many times greater than that of vinyl acetate.⁴² Although the copolymerization of DADMAC with hydrophobic monomers is inherently difficult, it is of continued interest because of the potential to impart the good physical properties of many vinyl homopolymers. Poly(methyl methacrylate) (PMMA), for example, forms films with high strength, flexibility, and optical clarity.⁴³ Despite the potential benefits of copolymers of PMMA, there are few literature reports of the copolymerization of DADMAC and methyl methacrylate (MMA) or other (meth)acrylate monomers. In 2014, DADMAC was copolymerized with hydroxyethyl acrylate followed by an emulsion copolymerization with MMA and butyl acrylate.⁴⁴ Amphiphilic materials were possible due to the inclusion of hydroxyethyl acrylate as a compatibilizing comonomer. The more conventional copolymerization of DADMAC and MMA has also been carried out in dimethyl sulfoxide (DMSO).⁴⁵ Copolymerization reactions were carried out over a range of temperatures and feed ratios and monitored by ¹H NMR spectroscopy. Although the polymerization did produce random copolymers, the reactivity ratios reported for the two monomers were dramatically different, resulting in the incorporation of predominantly MMA even at high DADMAC feed ratios. The poor composition control offered by copolymerization in DMSO resulted in little ability to tune properties like charge density and made it an ineffective method for synthesizing copolymer materials.

Anion exchange of DADMAC can produce a cationic monomer suitable for copolymerization with vinyl monomers. The anion exchange from chloride to hexafluorophosphate (PF₆) has been shown to result in a polymerizable form of the monomer that is hydrophobic and organic soluble.⁴⁶⁻⁴⁸ We determined that DADMA(PF₆) is highly soluble in MMA monomer, allowing for bulk copolymerization. Because bulk polymerization eliminates the occurrence of chain transfer to solvent, it favors higher molecular weight and promotes better monomer incorporation.^{49,50} We have developed a method for the bulk copolymerization of DADMA(PF₆) and MMA using azobisisobutyronitrile (AIBN) as a radical initiator. The objective of this work was to utilize this unique copolymerization method to produce water-

insoluble polymers containing diallyldimethylammonium units capable of forming films with good properties.

2.3 Experimental

2.3.1 Materials

MMA, received from Aldrich (99 % with 10-100 ppm MEHQ as inhibitor), was washed three times with 5 % NaOH(aq) then three times with DI water before being distilled over CaCl₂ under N₂ and stored under N₂ in a freezer until use. DADMAC was purchased from TCI America as a 60 % aqueous solution and used as received. Commercially synthesized, high molecular weight ($M_w \sim 400,000-500,000$) PDADMAC as a 20 wt. % aqueous solution was used as received from Aldrich. Anhydrous N,N-dimethylformamide (DMF) was purchased from VWR and distilled under reduced pressure from magnesium sulfate before use. AIBN (98 %) was obtained from Aldrich and recrystallized twice from acetone and dried under vacuum. A stock solution was prepared in DMF (0.50 mL, 0.061 mmol). Potassium hexafluorophosphate (KPF₆) was obtained from Aldrich and used without further purification. Deuterated dimethyl sulfoxide (DMSO-d₆) was purchased from Cambridge Isotope Laboratories, Inc. All other solvents and chemicals were used as received from commercial sources.

2.3.2 Characterization

Final polymer compositions and structures were determined by ¹H NMR spectroscopy on a JEOL ECA-500 FT-NMR. NMR samples of the polymer were prepared by transferring a massed sample of approximately 0.05 g of the copolymer to an NMR tube and adding 0.50 mL of DMSO-d₆. All peak shifts were referenced to residual solvent peaks. Infrared characterization was carried out on a Nicolet iS50 FTIR spectrometer by placing polymer films directly on the ATR crystal. PMMA molecular weight was determined by gel-permeation chromatography (GPC) employing a Viscotek GPC Max VE 2001 GPC solvent/sample module, a Thermo SpectraSYSTEM RI-150, and a Viscotek 270 dual detector. Separation occurred in two PolyPore PLgel mixed-D columns at a THF flow rate of 1 mL/min. The GPC molecular weight calculation was calibrated from a linear series of polystyrene standards and checked for accuracy using a PMMA standard of known molecular weight (M_w 350,000 g mol⁻¹).

2.3.3 Ion Exchange of DADMAC to DADMA(PF₆)

To exchange DADMAC from the chloride counterion to hexafluorophosphate (DADMA(PF₆)), a volume of the aqueous DADMAC solution was poured into an excess of a saturated aqueous solution of potassium hexafluorophosphate (KPF₆). A gel-like layer formed immediately, which became solid after a short cooling period and was isolated by vacuum filtration and washed thoroughly with DI water. The white, water insoluble DADMA(PF₆) was dried at room temperature under vacuum for at least 16 hours immediately before use. ¹H NMR ((CD₃)₂CO with residual (CH₃)₂CO (δ 2.02), 500 MHz): 6.02 (2H, m), 5.62 (4H, q), 3.87 (4H, d), 2.92 (6H, s).

2.3.4 Bulk Polymer Synthesis

Poly(DADMA(PF₆)-*co*-MMA) was synthesized with six feed ratios to target specific weight percent incorporation of DADMA(PF₆). A standard initiator solution was prepared by dissolving 0.1005 g AIBN in DMF in a 5 mL volumetric flask. A representative copolymerization procedure is as follows: a 10 mL pressure vial was charged with a stir bar and 1.0001 g (3.6878 mmol) DADMA(PF₆) and sealed with a septum. 1.05 mL (9.86 mmol) MMA and 0.10 mL of the AIBN solution (2.01 mg, 0.012 mmol AIBN) was added by syringe transfer. The reaction mixture was degassed by three freeze-pump-thaw (FPT) cycles using a dry ice/acetone bath then placed under a N₂ atmosphere. The pressure vial was then lowered into a 70 °C oil bath with stirring for 24 hours.

After 24 hours, the solution had become a hard, transparent, colorless plug. 2 mL of DMF was added to the pressure vial and left overnight to promote swelling of the polymer. Because of the solidity of the polymer plug and low surface contact area between the polymer and DMF in the pressure vial, the polymer did not readily dissolve. Instead, the polymer sat in DMF until significantly swollen and was then transferred to methanol and allowed to sit in the nonsolvent to ensure the solid polymer product could be isolated by filtration. After filtration, the polymer was dried at 60 °C under vacuum. To remove residual monomer, the isolated polymer was dissolved entirely in DMF to produce a viscous solution, crashed out in methanol, filtered, and dried (1.2924 g, 65 % yield).

HomoPMMA and homoPDADMA(PF₆) were synthesized in much the same way, but only one monomer was used. A 10 mL pressure vial was charged with MMA (1.0 mL) or DADMA(PF₆) (0.9997 g) and the AIBN solution (0.050 mL). The vial was degassed via three

FPT cycles then placed under N₂ atmosphere. The DADMA(PF₆) vial was placed into a warm water bath during thaw cycles until full melting of the monomer had occurred. The reactions were carried out for 24 hours at 70 °C then worked up using the same method as for the copolymers (PMMA: 0.7305 g, 78 % yield; PDADMA(PF₆): 0.2231 g, 22 % yield).

Films of all copolymers were cast from DMF. A solution of approximately 10 wt. % copolymer was made and pipetted onto a microscope slide. The slide was covered with a watch glass and heated until all solvent had evaporated. Films were delaminated from the slide by submersion in DI water.

2.3.5 Study of Polymer Composition Over Time

A 25 mL conical flask was charged with DADMA(PF₆) (4.4151 g, 16.280 mmol), MMA (5.90 mL, 55.4), and AIBN in DMF solution (0.50 mL, 0.061 mmol) then degassed by three FPT cycles and placed under N₂ atmosphere. Five 10 mL pressure vials were septum sealed and sparged with N₂. To each of the vials, 0.70 mL of the stock monomers solution was added. A small aliquot of the solution was taken for feed ratio analysis by NMR spectroscopy. A pressure vial was placed in a 70 °C oil bath for each of the following times: 30 minutes, 1 hour, 2 hours, 4 hours, and 24 hours. At the end of the reaction time, the vial was opened to air and approximately 2 mL of DMF was added. The polymer was precipitated in methanol, collected by vacuum filtration, dried under vacuum, mass yield determined, and analyzed by NMR spectroscopy.

2.3.6 Soxhlet Extractions

For all extractions, a 100 mL round bottom flask with boiling chips, a single thickness cellulose extraction thimble, and the respective polymer sample(s) were dried under vacuum at 80 °C overnight. All other glassware was dried in a glassware oven overnight. A mass of polymer was placed into the thimble, which was placed in a Soxhlet extractor connected to a water-cooled condenser. The round bottom flask was charged with approximately 70 mL of chloroform and heated to reflux using a heating mantle. The extraction was carried out for 24 hours, after which the chloroform was removed by rotary evaporation. The flask and thimble were each vacuum dried as before and the mass of each was measured again to determine the mass extracted and mass retained. NMR spectroscopy was performed on all fractions.

2.4 Results and Discussion

This research aimed to synthesize a series of copolymers containing MMA and a diallyldimethylammonium monomer of controllable composition. The bulk polymerization afforded by the solubility of DADMA(PF₆) in MMA was hypothesized to lead to more equal monomer incorporation that would produce materials capable of forming stable, flexible, cationic films. The bulk polymerization method developed herein is notable because it allows for the controllable copolymerization of an ionic vinyl monomer with a hydrophobic vinyl monomer. The strength, flexibility, and water stability of the resulting materials is also unusual for polymers containing diallyldimethylammonium units in the backbone.

2.4.1 Ion Exchange

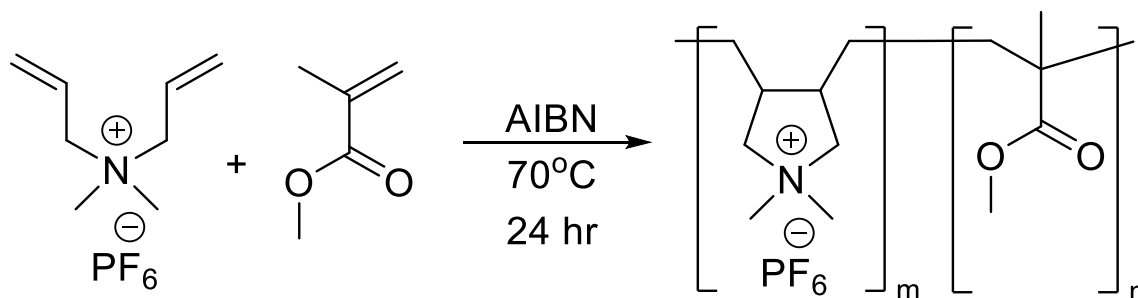
Counterion exchange to PF₆ was chosen because the bulky, fluorine containing ion is much less hydrophilic than chloride. Conversion from Cl to PF₆ was a facile and reproducible process. Dramatic solubility changes were observed after the anion exchange. In contrast to the hydrophilic DADMAC, the PF₆ monomer salt is highly insoluble in water and soluble in polar aprotic solvents such as DMF, dimethyl acetamide, *N*-methyl-2-pyrrolidone, and DMSO. After ion exchange, a strong PF₆ peak can be observed by FTIR at 827 cm⁻¹, which was not present in the chloride form. Although mass balance analysis indicated that only 60-70 wt. % of the material was both ion exchanged and collected, the solubility and FTIR analysis indicate that all of the collected monomer was in the PF₆ form. Most significantly, DADMA(PF₆) was found to be miscible with MMA, even at majority DADMA(PF₆) by weight. Ion exchange to other counterions, such as thiocyanate and tosylate were also performed. However, the exchange to PF₆ produced the most distinctly hydrophobic monomer. As a result, the PF₆ form of the monomer proved to be the easiest to isolate and purify, and all polymerizations were carried out using DADMA(PF₆).

2.4.2 Polymer Synthesis

To determine a reasonable synthesis procedure, both MMA and DADMA(PF₆) were polymerized under the same set of conditions. AIBN was chosen as the radical initiator because it is known to be an effective initiator for the homopolymerization of MMA.⁵⁰⁻⁵² To allow for the repeat addition of exact amounts of AIBN, the initiator was added in the form of a standardized stock solution in DMF. While this did introduce some solvent to the system, the low

concentration of DMF relative to the monomers still effectively reduced chain transfer to solvent and allowed the reaction to be characterized as “bulk.” To produce the homopolymers, a pressure vial was charged with a stir bar, the monomer of interest, and a volume of the initiator solution. The vial was then degassed through a freeze-pump-thaw process to remove oxygen and prevent the evaporation of MMA. Polymerization was carried out at 70 °C for 24 hours to ensure complete conversion based on AIBN kinetics.^{53,54} Both homopolymers were successfully synthesized through this method. PMMA was produced at a 78 % yield and found to have a number average molecular weight (M_n) of 359,000 g mol⁻¹ by GPC with respect to polystyrene standards. The PDADMA(PF₆) produced was of high enough molecular weight to form films but only a low polymer yield (22 %) was achieved.

A series of copolymers was produced using the same procedure (Scheme 2.1). A measured amount of each monomer was added to a pressure vial followed by the AIBN solution, the reaction mixture was degassed through the freeze-pump-thaw method, and the polymerization was carried out under inert atmosphere at 70 °C. The feed ratios of MMA and DADMA(PF₆) were chosen to incorporate a range of DADMA(PF₆) compositions by weight, from 20 wt. % DADMA(PF₆) (D20) to 80 wt. % DADMA(PF₆) (D80) (Table 2.1) At concentrations of DADMA(PF₆) above 80 wt. %, the ammonium monomer could not be fully dissolved in the small amount of MMA. All syntheses were carried out with approximately 2 g total monomer and 0.00201 g of AIBN dissolved in 0.1 mL DMF.



Scheme 2.1 The copolymerization of DADMA(PF₆) and MMA.

Table 2.1 Series of reaction trials showing the relative masses and concentration of both monomers in the copolymer feed.

Trial	MMA			DADMA(PF ₆)		
	Mmole	Mass (g)	Mmole	Mass (g)	Mole %	Mass %
D20	16.0	1.60	1.48	0.400	8.5	20
D30	14.1	1.41	2.21	0.600	14	30
D40	12.2	1.22	2.95	0.800	19	40
D50	10.0	1.00	3.69	1.00	27	50
D60	7.98	0.80	4.42	1.20	36	60
D70	6.10	0.61	5.16	1.40	46	70
D80	4.04	0.40	5.90	1.60	59	80

Polymer was successfully synthesized across all feed ratios under the same reaction conditions. Within 24 hours at 70 °C, all reaction solutions hardened into solid, clear, colorless plugs. The solids were submerged in a few mL of DMF, heated gently, and allowed to sit for at least 24 hours. The polymers of higher DADMA(PF₆) ratios took notably longer times to swell in DMF. Once all the polymers had softened, the highly viscous, polymeric DMF solutions were poured slowly into stirring methanol. For all trials, a white solid precipitate formed immediately and was collected by vacuum filtration.

2.4.3 Determination of Copolymer Composition

The ratio of MMA to DADMA(PF₆) units incorporated in the final copolymer was determined by ¹H NMR spectroscopy in DMSO-d₆. Although the polymeric nature does lead to peak broadening, both the MMA and DADMA(PF₆) units demonstrate characteristic peaks with high enough resolution to determine relative ratios (Figure 1.1). Two peaks at approximately 0.7 and 0.9 ppm result from the methyl protons of atactic PMMA. The methyl protons of the dimethyl ammonium moiety in DADMA(PF₆) ring led to a set of peaks at approximately 3.05 and 3.15 ppm. By integrating the characteristic peaks and comparing their relative values, it is possible to determine the relative molar and therefore mass composition of the synthesized copolymers (Figure 2.2).

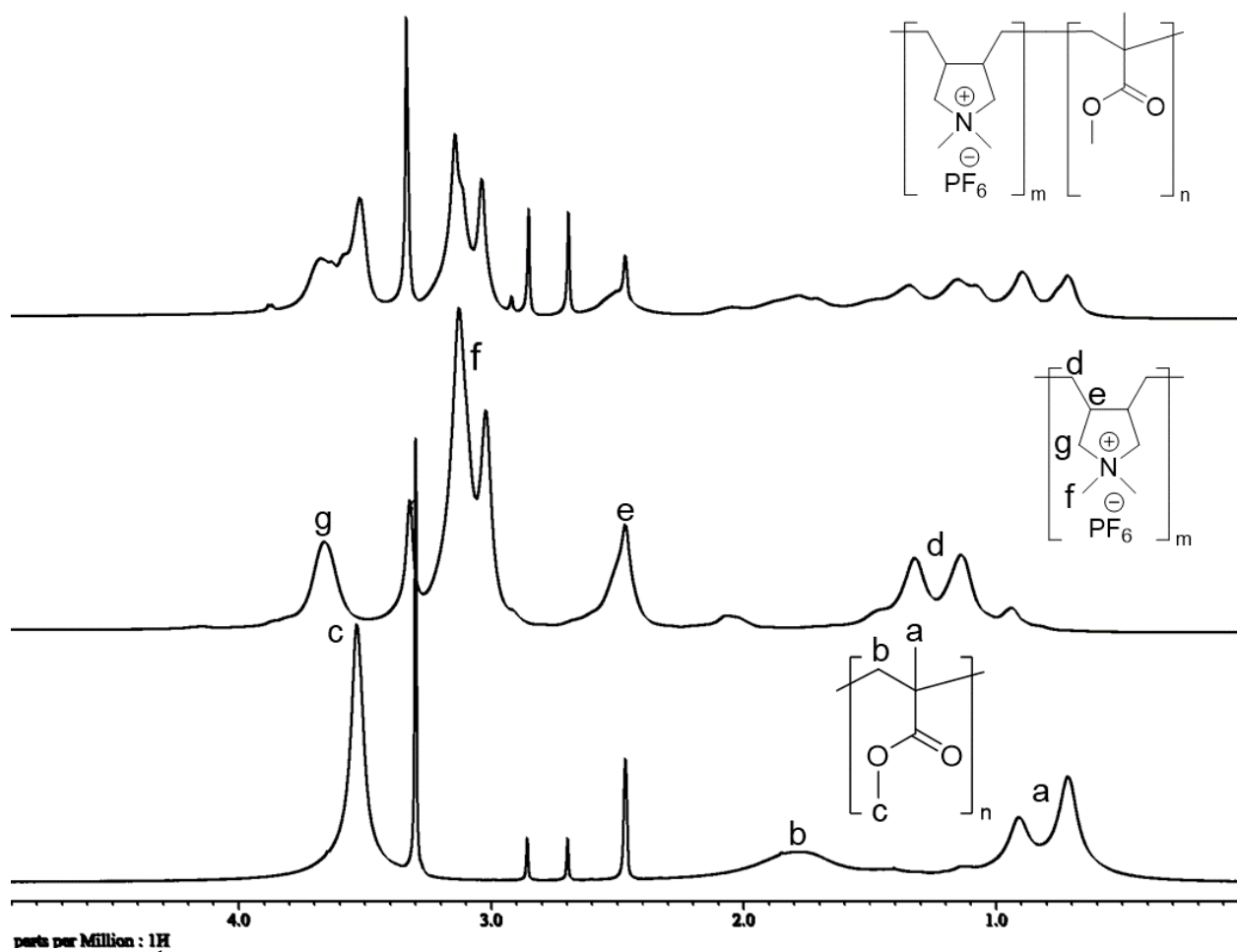


Figure 2.1 ^1H NMR spectra of PMMA homopolymer (bottom), PDADMA(PF_6) homopolymer (middle), and D80 copolymer (top).

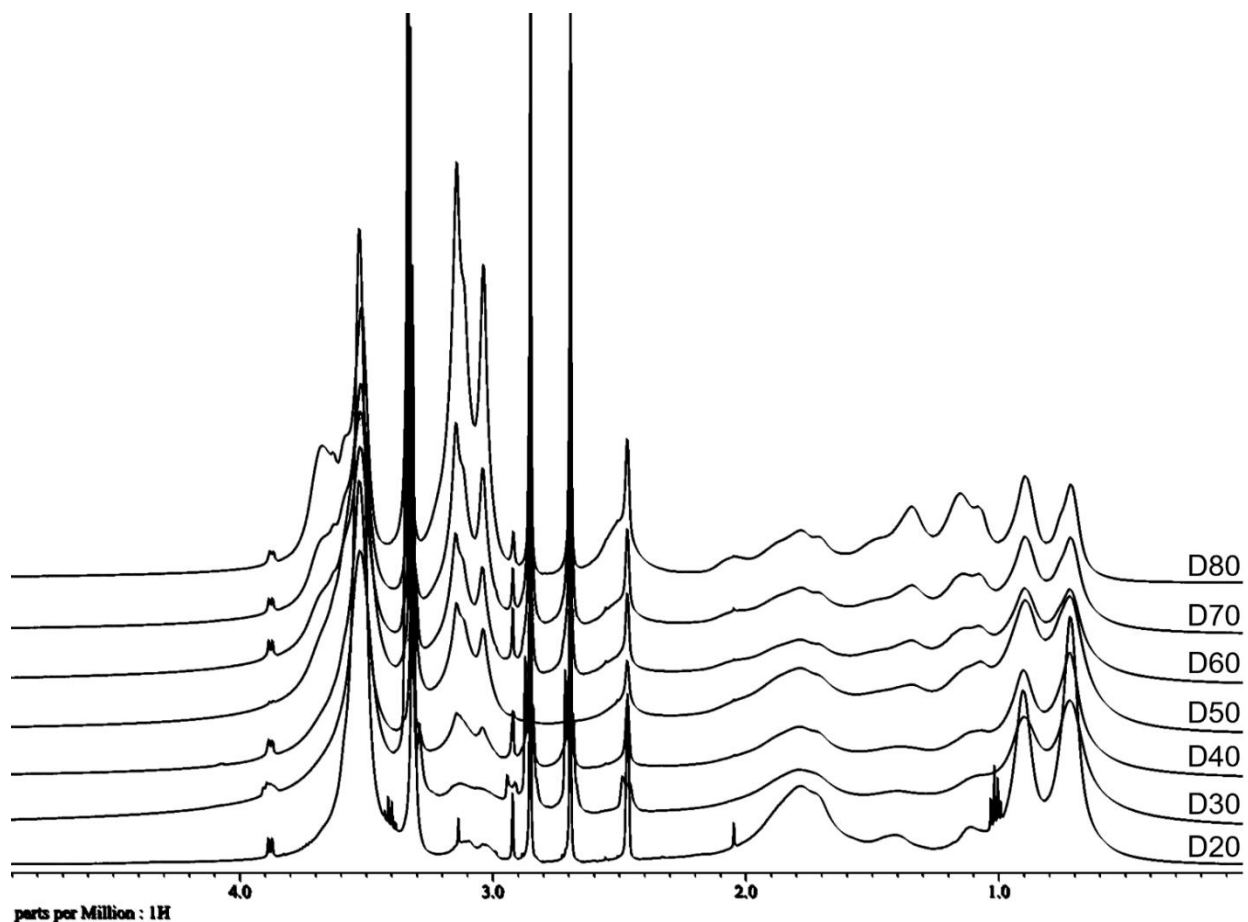


Figure 2.2 ^1H NMR spectra of all copolymer compositions.

Table 2.2 Composition of copolymers after 24 hours of reaction time as determined by ^1H NMR spectroscopy.

Trial	Monomer feed		Copolymer product	
	Mol% DADMA(PF ₆)	Mass% DADMA(PF ₆)	Mol% DADMA(PF ₆)	Mass% DADMA(PF ₆)
D20	8.5	20	4.2	11
D30	14	30	9.5	22
D40	19	40	14	30
D50	27	50	20	40
D60	36	60	30	53
D70	46	70	38	63
D80	59	80	57	78

The feed ratios of the two monomers were shown to correlate to the composition of the final copolymers (Table 2.2). As the ratio of DADMA(PF₆) in the monomer feed was increased, there was a corresponding increase in the relative amount of DADMA(PF₆) units incorporated in the final copolymer (Figure 2.3). However, a linear fit of the data produces a calculated intercept that does not agree with the realities of copolymerization. When no DADMA(PF₆) is present in the monomer feed, no copolymer is produced, and the resultant copolymer composition would be 0 %. If the data is extrapolated to the end points of (0,0) and (100,100), the data is better fit by a curved line (Figure 2.4). The specific shape of the line is characteristic of a system in which the reactivity ratio of one monomer is greater than one and the reactivity ratio of the other is less than one.⁵⁵ For the bulk MMA/DADMA(PF₆) system, it is predicted that the reactivity ratio of DADMA(PF₆) (r_D) is less than one and that of MMA (r_M) is greater than one. If this is the case, it would be expected that both the growing chains capped by DADMA(PF₆) radicals and those capped by the MMA radicals would favor the addition of an MMA monomer unit. Due to the small deviation of the curve from a linear fit line, it can be assumed that the addition of the MMA is only slightly favored. Therefore, it is possible to produce copolymers with high levels of DADMA(PF₆) incorporation.

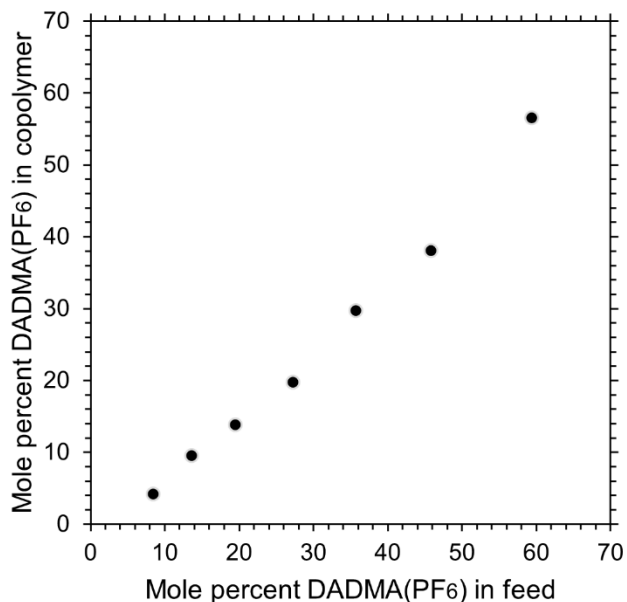


Figure 2.3 Copolymer composition as a function of feed ratio.

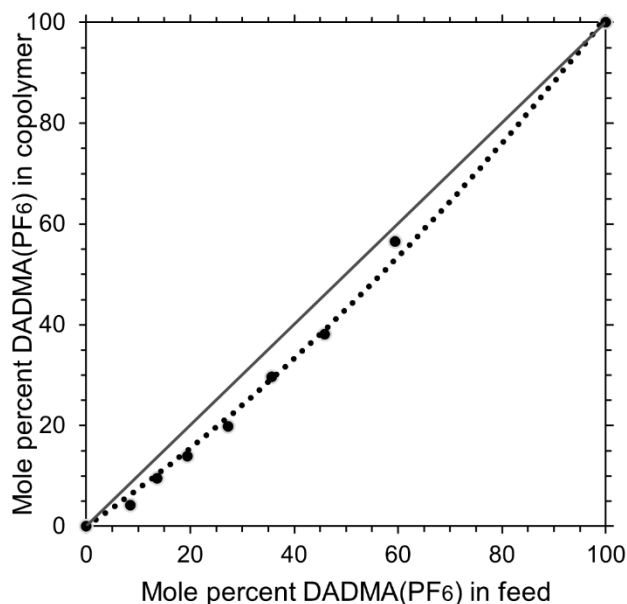


Figure 2.4 Curved fit line for the mole percent composition data extrapolated to (0,0) and (100,100) intercepts. Solid line represents the anticipated result for a system of equal reactivity ratios.

Attempts to quantify the reactivity ratios in this system proved difficult due to the limited characterization options for the ionic species DADMA(PF₆) and PDADMA(PF₆). To use the Mayo-Lewis, Fineman-Ross, or Kelen-Tudos methods to calculate reactivity ratios, it is necessary to accurately determine the copolymer compositions at very low conversion.⁵⁶ Quantitative determination of such small concentration changes is inherently difficult, which is compounded when unequal reactivity ratios in a system cause one monomer to have especially low incorporation into the copolymer. When the copolymerizations were stopped at low conversion and analyzed by NMR spectroscopy, the change in concentration of the DADMA(PF₆) monomers was too small to be reproducibly quantified, further supporting the assumption that the reactivity ratio of MMA is higher than that of DADMA(PF₆). Although in a previous report the reactivity ratios of DADMAC and MMA were calculated from in-situ NMR spectroscopy data,⁴⁵ the bulk nature of our copolymerization makes it unsuitable for in-situ spectroscopy. When GC/MS was investigated as a mechanism for calculating small monomer changes in the low conversion copolymerizations, MMA concentrations were easily determined but the ionic monomer species cannot move through the GC column. Due to the inability to calculate numerical reactivity ratios, we chose other characterization techniques to further understand the copolymerization results.

2.4.4 Soxhlet Extractions

To ensure that copolymer was being synthesized rather than a blend of homopolymers, Soxhlet extractions were carried out on some of the copolymer samples. Chloroform was selected as the solvent since it effectively extracts homoPMMA but not homoPDADMA(PF₆). This was demonstrated by preparing an approximately 50:50 blend of the two homopolymers and performing Soxhlet extraction. Only PMMA is found to be extracted by NMR spectroscopy and the amount extracted and retained is in that same 50:50 ratio. The Soxhlet extraction results (Table 2.3) support the conclusion that increased amounts of DADMA(PF₆) in the monomer feed produces copolymer with higher amounts of DADMA(PF₆) units. When extraction was performed on the D20 sample, nearly all the sample was extracted into the chloroform. ¹H NMR evaluation of the extracted material indicated it had the same composition as the isolated copolymer sample prior to extraction. In contrast, for the D80 sample, only a small amount of the copolymer was extracted. The extracted material demonstrated NMR signals characteristic of both MMA and DADMA(PF₆) repeat units, though the relative concentration of MMA repeat units was found to be much higher than in the initial copolymer sample. For the intermediate copolymer composition, essentially equal amounts of the material were extracted and retained. Once again, the extracted material was enriched in MMA and the retained material was enriched in DADMA(PF₆). The solubility of the copolymers was dramatically different from that of the homopolymers, with low amounts of DADMA(PF₆) allowing for solubility in chloroform while larger amounts of DADMA(PF₆) were needed to avoid solubility. For MMA to be present in the retained polymer mass after extraction, it must have been present in a copolymer that also contains the insoluble DADMA(PF₆) units. Conversely, for DADMA(PF₆) to be present in the extracted material, it was necessarily in the form of copolymer with the soluble MMA. Therefore, significant portions of both the extracted and retained mass of all tested compositions must have been copolymer rather than either homopolymer. However, the difference in composition between the extracted and retained polymer materials indicate notable heterogeneity within the copolymer sample. The presence of copolymer with different compositions within one sample also points to unequal reactivity ratios and expected compositional drift during polymerization.

Table 2.3 Soxhlet extraction results.

Homopolymer blend					
Mass PMMA (g)	Mass DADMA(PF ₆)	Extracted mass (g)	Retained mass (g)		
0.1165	0.1023	0.1198	0.1037		
Copolymers					
Trial	Initial Mass (g)	Extracted Mass (g)	Retained Mass (g)	Extracted Mass (%)	Retained Mass (%)
D20	0.2087	0.2147	0.0060	97	3
D50	0.2107	0.1066	0.1060	50	50
D80	0.2043	0.0411	0.1572	21	79

2.4.5 Copolymer Composition Over Time

Given the heterogenous nature of the copolymers and the hypothesized difference in reactivity ratios, we would expect composition drift over the course of the reaction. At low conversion, when concentrations of both monomers are high, growing chains will prefer to add MMA monomer and the resulting polymers will be enriched in MMA. As MMA is preferentially added, the concentration of MMA will decrease faster than that of DADMA(PF₆). Eventually the discrepancy in monomer concentration will overcome the effect of the inequality in reactivity ratios, causing more DADMA(PF₆) to be incorporated.

To test this, a stock solution of 24 mole % DADMA(PF₆) was made and analyzed by ¹H NMR spectroscopy. Aliquots of the stock solution were then prepared and polymerized using the same procedure as above except that the reactions were stopped after 0.5, 1, 2, 4, and 24 hours. The incorporation of DADMA(PF₆) in the resulting copolymers was found to increase quickly then level off (Figure 2.5). Figure 5 captures the amount of DADMA(PF₆) in the entire isolated sample, thus capturing the composition of all copolymers produced up to the particular reaction time. The copolymers produced at low conversion are significantly enriched in MMA. Conversion quickly increases, and with it so does the percentage of DADMA(PF₆) in the copolymer product. This supports the conclusion that r_D is less than one and r_M is greater than one, but that the overall final composition at high conversions is close to the feed amount.

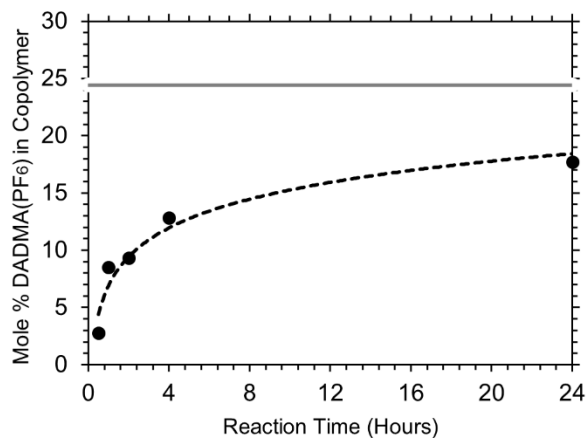


Figure 2.5 Copolymer composition as a function of time for constant feed ratio. Percent yields with respect to the 24 hour sample were as follows: 5 % at 0.5 hr, 12 % at 1 hr, 88 % at 2 hr, 91 % at 4 hr, 100 % at 24 hr.

2.4.6 Film Casting and Properties

As the homopolymer, PDADMA(PF₆) forms only brittle, fragile, and cloudy films. Conversely, PMMA homopolymer is well known for its ability to produce films with excellent strength, flexibility, and clarity. To determine the properties of the copolymers, films were cast from approximately 10 wt. % of each polymer in DMF. After the films were formed, they were delaminated from the glass slides by submersion in water. Qualitative examinations of the free-standing films showed a correlation between the concentration of DADMA(PF₆) in the polymer and the film properties. At lower concentrations of DADMA(PF₆), the films have properties like those of PMMA. The D20 film showed good strength, flexibility, and creasability. Like PDADMA(PF₆), the film of D80 was very brittle. Films of intermediate compositions demonstrated properties between those of the two homopolymers. The low concentration DADMA(PF₆) films also have excellent optical clarity (Figure 2.6). At higher DADMA(PF₆) concentrations, notably D70 and D80, the films have some cloudiness, similar to the PDADMA(PF₆) films. The cloudiness may result from microphase separation occurring between polymer chains with more blocky character, which would be possible as the copolymer composition varies more from homoPMMA. In comparison, a film cast of a 50 wt. % DADMA(PF₆) blend of the two immiscible homopolymers was significantly cloudy, heterogenous in appearance, and very brittle. The relative clarity and flexibility of the copolymer films relative to the blends further supports their identity as copolymers. Unlike PDADMAC, the copolymer films over all compositions show no notable dissolution after extended periods of

time submerged in water. The ability of the copolymers to form stable stand-alone films opens the possibility of membranes and coatings for aqueous applications.

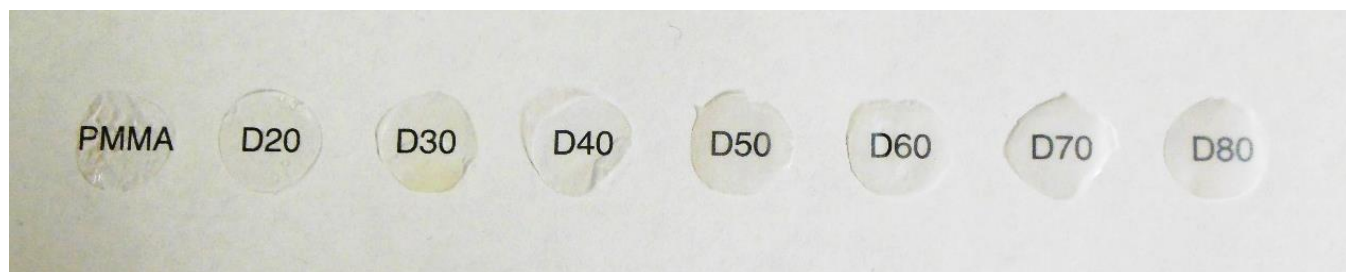


Figure 2.6 Films of PMMA and copolymers D20-80.

2.5 Conclusions

This research presents the synthesis of P(DADMA(PF₆)-*co*-MMA) via bulk radical copolymerization using AIBN as an initiator. The one-step, one-pot synthesis produced copolymer from a range of comonomer feed ratios. This is the first report of the radical copolymerization of MMA with a diallyldimethylammonium monomer where a significant amount of the ammonium monomer was incorporated into the polymer chain. In addition, the bulk synthesis leads to a good relationship between the composition of the comonomer feed and final copolymer allowing for significant tunability of composition. Soxhlet extractions demonstrate that there is not a significant portion of homopolymer present in the samples, but there is heterogeneity in copolymer composition. A study of copolymer composition over reaction time demonstrated significant composition drift where the incorporation of MMA was higher at lower conversions. The copolymer characterization indicates that the reactivity ratio of MMA is higher than that of DADMA(PF₆), but the reaction system is still capable of forming copolymers containing a high ratio of DADMA(PF₆). All synthesized polymers were of sufficient molecular weight to form stand-alone films. Those of low DADMA(PF₆) incorporation had properties similar to that of PMMA while films from polymers with high concentrations of DADMA(PF₆) were more akin to PDADMA(PF₆). The D20 and D30 films, which contained 11 and 22 wt. % DADMA(PF₆) respectively, demonstrated good strength, flexibility, and optical clarity while still maintaining the inherent cationic nature of PDADMA(PF₆). Bulk copolymerization provides a novel one-pot method for synthesizing copolymers with good physical properties and tunable charge density from inexpensive and widely available materials.

2.6 References

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CHAPTER 3

SYNTHESIS AND INITIAL CHARACTERIZATION OF POLYDIALLYLAMMONIUM-POLYSULFONE MULTIBLOCK COPOLYMERS FOR MOISTURE SWING CO₂ UPTAKE

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3.1 Abstract

Polysulfones are an important class of materials for a variety of applications due to their excellent strength and stability. Quaternary ammonium polymers are also useful materials due to their conductivity and ion exchange properties. Copolymers containing both these functionalities would have a combination of properties that would be of interest for a variety of applications. In this study, a series of multiblock copolymers containing both diallyldimethylammonium blocks and polysulfone blocks were synthesized. Telechelic poly(diallyldimethylammonium hexafluorophosphate) (PDADMA(PF₆)) oligomers were synthesized using bis(4-aminofluoro)disulfide as an iniferter molecule. The resultant fluorophenylsulfone-capped oligomers were then reacted in-situ with bis(4-fluorophenyl)sulfone and bisphenol A. The resultant multiblock copolymers were synthesized at high yield over a range of compositions, and films with good flexibility and strength were formed from most of the copolymer compositions. Initial testing of the copolymer materials for moisture-swing, direct-air CO₂ capture indicated some promise in this field though significant further study and optimization would be necessary to produce commercially viable materials.

3.2 Introduction

Since the synthesis of the first polysulfone (PSf) in the 1960s, polysulfones have become an increasingly studied and used class of thermoplastics known for their excellent thermal and chemical stability.¹ The exceptional properties of polysulfones, specifically aromatic polysulfones, have led to their application in fields including nanofiltration, energy storage, and

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biochemical separations.²⁻⁵ To produce polysulfone membranes with improved properties for specific applications, several copolymers and functionalized polysulfones have been developed.⁶

The introduction of charged groups into polysulfones produces materials with particularly interesting properties. Due to the hydrophobic nature of polysulfones, they are prone to fouling during use in membrane purification applications. The functionalization of polysulfones with cationic groups through processes like grafting has been shown to reduce the affinity of the polymer surface for contaminants and therefore increases membrane performance.⁷ Cationic polysulfones are also interesting for their ability to serve as anion exchange membranes. Materials in which the cationic functionalities are paired with hydroxide counterions have demonstrated good hydroxide ion conductivity, making them promising materials for applications including anion exchange membrane fuel cells.^{8,9} While numerous cationic groups are available, quaternary ammonium groups are often favored due to the variety of chemistries and high stabilities that can be achieved.^{10,11}

When producing membranes with transport or conductivity properties, polymer morphology is crucial, and the presence of ion channels is known to improve membrane performance.^{3,12,13} Ion channels are achieved through the introduction of structured side chains or blocks with different polarity from the rest of the polymer backbone, which will cause the polymer chains to align during membrane formation, leading to microphase separation. Multiblock copolymers containing a hydrophobic polysulfone block and cationic block have been shown to undergo the necessary microphase separation to achieve high ion conductivity.⁸ Polydiallyldimethylammonium blocks are of interest due to the increased alkaline stability that results from their cyclopolymerization,^{14,15} which makes the polymer more suitable for applications where hydroxide ion concentration is high.

The same properties that make cationic polysulfone polymers suitable anion exchange membranes make them of interest as direct-air CO₂ capture membranes. Direct-air CO₂ capture is a process of newfound importance as it becomes increasingly clear that negative CO₂ emission will be necessary to slow climate change to desired levels.^{16,17} Quaternary ammonium membranes with hydroxide counterions have a natural affinity for carbon dioxide due to the chemical equilibrium between carbonate, bicarbonate, and hydroxide ions.^{18,19} When a membrane is dry, CO₂ is absorbed as hydroxide counterions are converted to bicarbonate and carbonate counterions. As humidity is increased, the high concentrations of water favor the

bicarbonate over carbonate counterions, and CO₂ is released. The use of “moisture-swing” chemical absorption and desorption offers benefits over other direct-air CO₂ capture techniques because it relies on changes in relative humidity rather than the input of high levels of energy.²⁰

The objective of the work presented in this chapter was the development and characterization of stable, cationic multiblock polysulfones. To provide for this, it was necessary to determine a synthetic method that allowed for the compatibilization of polymer materials with different polarities and different polymerization mechanism. The chosen base stable, quaternary ammonium monomers, diallyldimethylammonium salts, are polymerized via radical reactions but polysulfones are produced through nucleophilic aromatic substitution condensation polymerizations. To form multiblock copolymers, difunctionalized ammonium oligomers were made using an iniferter-based synthesis, then reacted in-situ with the required monomers to produce polysulfones. Preliminary moisture-swing, direct-air CO₂ capture testing was performed with membranes of the copolymers, which indicated some promise for the materials but less than desirable final performance.

3.3 Methods

3.3.1 Materials

4-fluorothiophenol (98 %) was purchased from Aldrich and used as received. Diallyldimethylammonium chloride (DADMAC) was obtained from TCI America as an approximately 60 % aqueous solution and was used as received. Bis(4-fluorophenyl) sulfone (99 %) and bisphenol A (BPA) (97 %) were received from Aldrich, twice recrystallized from toluene, and dried under vacuum immediately before use. N,N-dimethylacetamide (DMAc) (99 %) was purchased from Aldrich, distilled under reduced pressure, and stored under N₂. Potassium hexafluorophosphate (KPF₆) (98 %) and potassium carbonate (K₂CO₃) (100 %) were used as received from Aldrich. Deuterated dimethyl sulfoxide (DMSO-d₆) (99.8 %) was purchased from Cambridge Isotopes, Inc. Iodine crystals (USP grade) were used as received from Fischer. All other chemicals and solvents were obtained from commercial sources and used without further purification. A model number SCT-4 UV pen lamp (25 amps, 115 volts) was obtained from Ultra-Violet Products, Inc.

3.3.2 Characterization

Final polymer compositions and structures were determined by ^1H NMR spectroscopy on a JEOL ECA-500 FT-NMR using DMSO-d_6 as solvent. Thermogravimetric analysis was carried out on a Seiko Instruments TG/DTA 320. Samples were heated under air to 100°C at 40°C per minute, held at 100°C for 5 to 10 minutes, then heated to 800°C at 10°C per minute before being cooled to room temperature. All runs were performed in a platinum pan with an empty platinum pan as reference. Differential scanning calorimetry (DSC) was performed on a TA Instruments Q20 DSC to measure thermal transitions. Samples in hermetically sealed T-zero aluminum pans were heated from 0°C to an appropriate maximum temperature between 230°C and 300°C at a rate of 10°C per minute then cooled back down to 0°C . Two cycles were completed and data from the second cycle was used to determine glass transition temperatures. All runs were completed under a 20 mL per min flow of N_2 with an empty T-zero aluminum pan as reference.

3.3.3 Synthesis of Bis(4-fluorophenyl)disulfide

The oxidation of 4-fluorothiophenol afforded bis(4-fluorophenyl)disulfide, as described in previously published work.⁸ A 50 mL round bottom flask was charged with a stir bar, DI water (10 mL), and methanol (10 mL). The addition of 4-fluorothiophenol (2.41 g, 18.8 mmol) produced two distinct layers. The flask was lowered into an ice bath and solid iodine (2.38 g, 9.40 mmol) was added in small portions over approximately 20 minutes. Upon addition of the iodine, the solution became cloudy and brown. After a period of rapid stirring, the brown color indicative of unreacted iodine dissipated, and a yellow-green oil formed. The oily bis(4-fluorophenyl)disulfide product was recovered by extraction (2.24 g, 93 % yield).

3.3.4 Synthesis of 4-Fluorothiophenol Capped PDADMAC Oligomers

The experimental concentration of the reported 60 % DADMAC in water solution was determined by Mohr titration to be 70.3 ± 0.2 % DADMAC by weight. Therefore, a 2.5 M DADMAC solution in $\text{H}_2\text{O}/\text{MeOH}$ was prepared by diluting the DADMAC solution (14.38 g, 0.0625 mol) to 25 mL with methanol. The iniferter and monomer concentrations were chosen to target oligomers of approximately 150 repeat units. Three 10 mL test tubes with stir bars were each charged with the 2.5 M DADMAC solution (8 mL, 20 mmol) followed by a 1 M bis(4-fluorophenyl)disulfide in methanol solution (0.13 mL, 0.13 mmol). All tubes were then septum

sealed and sparged with N₂ in ice for 30 minutes. They were then lowered into a 60 °C oil bath and allowed to temperature equilibrate for 10 min before being exposed to a 254 nm UV light for 48 hours. After 48 hours, the reaction tubes were removed from heat and UV and allowed to cool to room temperature before being opened to air. The clear, colorless solutions were poured slowly into stirring acetone to give a fine white precipitate. This was collected by vacuum filtration, dissolved in a small amount of methanol, reprecipitated in acetone, collected by vacuum filtration, and dried under vacuum at 60 °C overnight (5.19 g, 38 % yield). The oligomers were calculated to have 130 repeat units by ¹H NMR spectroscopy.

3.3.5 Oxidation and Ion Exchange of PDADMAC Oligomers

To oxidize the sulfide oligomer end groups to sulfones, the 5.19 g of functionalized oligomer was dissolved in approximately 25 mL of DI water in a 50 mL round bottom with stir bar. To this was added 0.0604 g Oxone (1.97 mmol, approximately eight times end group concentration). The mixture was stirred until homogenous then placed in a 60 °C oil bath for 18 hours. This was cooled to room temperature and concentrated to a viscous solution by rotary evaporation, which was then poured into a saturated solution of potassium hexafluorophosphate (KPF₆) to produce a white precipitate. The solid product was collected by vacuum filtration, washed with an excess of DI water, and dried under vacuum at 60 °C overnight (6.92 g, 87 % yield). Full oxidation was confirmed by ¹H NMR spectroscopy. ¹H NMR (500 MHz, DMSO-*d*₆, δ): 7.97 (d, 4H; Ar H), 7.54 (d, 4H; Ar H), 5.37 (bs, 2H; CH₂), 3.67 (bs, 4H; CH₂), 3.13 (m, 6H; CH₃), 2.47 (bs, 2H; CH), 1.13 (m, 4H; CH₂).

3.3.6 Synthesis of Multiblock Polysulfones

Block copolymers were synthesized following a modified procedure from previously published work.⁸ Four feed ratios were designed to target a range of PDADMA(PF₆) incorporation by weight percent. For all the synthesized block copolymers, the PDADMA(PF₆) oligomers with an average of 130 repeat units were used. A representative procedure is as follows: A two neck, 15 mL round bottom flask with stir bar was connected to a pre-filled Dean-Stark trap, water cooled condenser, and N₂ inlet. The flask was charged with BPA (0.4566 g, 2.000 mmol), K₂CO₃ (0.42 g, 3.00 mmol), toluene (2 mL), and DMAc (5 mL) and lowered into a 150 °C oil bath for 3 hours to remove water to the Dean-Stark trap. After 3 hours, the solution

was cooled to room temperature and bis(4-fluorophenyl)sulfone (0.5056 g, 1.989 mmol) and PDADMA(PF₆) (0.4000 g, 0.01135 mmol end groups) were added in quick succession. The Dean-Stark trap was removed, and the solution was brought to reflux for 24 hours under N₂. The viscous, cloudy, tan solution was cooled to room temperature, opened to air, and poured slowly into stirring methanol. The fibrous, white precipitate was isolated by vacuum filtration and washed with methanol. The dried product was then transferred to a 100 mL round bottom flask with approximately 70 mL of DI water and boiled overnight to remove residual salt. The polymer was again isolated by vacuum filtration, washed with DI water and methanol, and dried under vacuum at 60 °C overnight (1.17 g, 92 %).

3.3.7 Preparation of Polymer Films

To prepare nonporous films for testing, 0.21 g of each polymer was dissolved in 1.4 mL of DMAc and placed on a shaker overnight to dissolve fully. The viscous, slight cloudy solutions were passed through 1.5 µm syringe filters onto glass microscope slides. The solution was spread until the full slide surface was covered and the solvent was evaporated at approximately 75 °C over 30 minutes. The films were delaminated by submerging them in DI water. To ion exchange the films, they were first converted to the chloride form and then to the hydroxide form. The films were refluxed in saturated sodium chloride solution for 48 hours. After 48 hours, a characteristic PF₆ peak was still present in the FT-IR spectrum, so the films were refluxed in sodium chloride for an additional 48 hours. The films were rinsed with DI water then submerged in 2 M potassium hydroxide for 48 hours at room temperature. Finally, the films were submerged in six successive N₂ purged DI water baths, pH tested to ensure no residual potassium hydroxide was present, and dried under vacuum overnight.

3.4 Results and Discussion

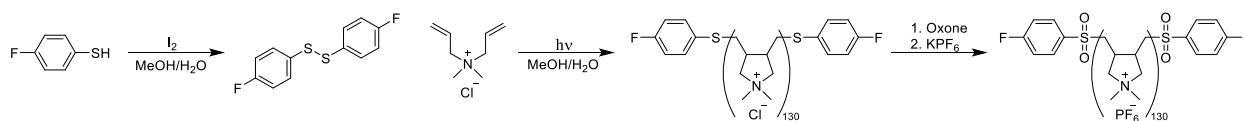
3.4.1 Synthesis of Functionalized PDADMA(PF₆) Oligomers

Iniferters are a unique class of molecules that function as radical initiators as well as chain transfer agents and terminators. Disulfide molecules are one useful class of iniferters.^{21,22} Upon exposure to UV-irradiation, the sulfur-sulfur bond cleaves to produce two sulfide radicals, which initiate chain growth polymerization. When functionalized disulfide iniferters are employed in the polymerization of DADMAC, the result is PDADMAC oligomers

functionalized on each end with groups resulting from the iniferter chemistry. Because the favored mechanism for termination in DADMAC polymerizations is recombination,²³ it was assumed that all oligomers were effectively difunctionalized. An additional benefit of iniferter-based syntheses is the ability to control the molecular weight of the oligomer by changing the ratio of iniferter to monomer during polymerization. The functionalized oligomers can then be used in a manner analogous to the difunctional monomers of a step-growth polymerization.

To produce oligomers suitable for the incorporation of polysulfones, bis(4-fluorophenyl)disulfide was chosen as the iniferter. The fluorophenyl sulfide capped PDADMAC oligomers were characterized by quantitative ¹H NMR spectroscopy by comparing the integration values of the peaks resulting from the methylene linkages of the DADMAC units (0.7-1.8 ppm) to the integration values of the aromatic peaks resulting from the end-groups (6.51 and 7.11 ppm) (Figure 3.1). The iniferter to monomer ratio employed in the synthesis was 1:150 and the resulting oligomers were found to have 130 repeat units.

The PDADMAC oligomers required some modification before being used in a polysulfone polymerization. Since the nucleophilic aromatic substitution reaction used to make polysulfones is promoted by resonance structures involving the sulfone group, it was necessary to oxidize the sulfide end-groups of the oligomers to sulfones. The final modification was to address the solubility issues that arose from the hydrophilicity of the PDADMAC oligomers. Polysulfone syntheses require polar aprotic solvents, which are not good solvents for PDADMAC. It has been previously demonstrated that exchange of the chloride for other counterions can significantly impact the solubility of both DADMAC and PDADMAC.²⁴ We determined that the ion exchange from chloride to hexafluorophosphate produces oligomers that are not only entirely insoluble in water but have good solubility in polar aprotic solvents. The fluorophenyl sulfide capped PDADMA(PF₆) oligomers are suitable for use in polysulfone synthesis procedures.



Scheme 3.1 The synthesis of telechelic PDADMA(PF₆) oligomers.

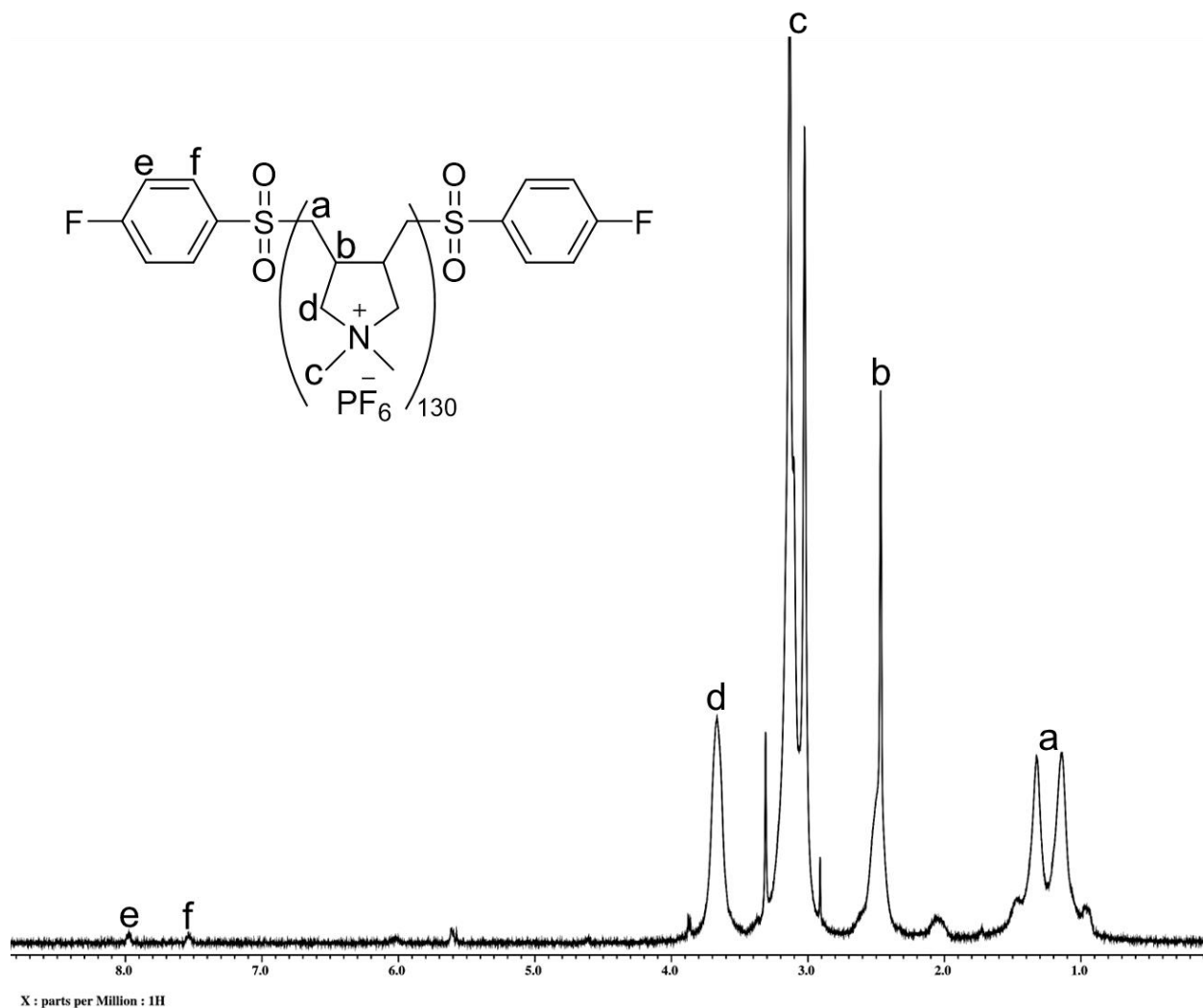
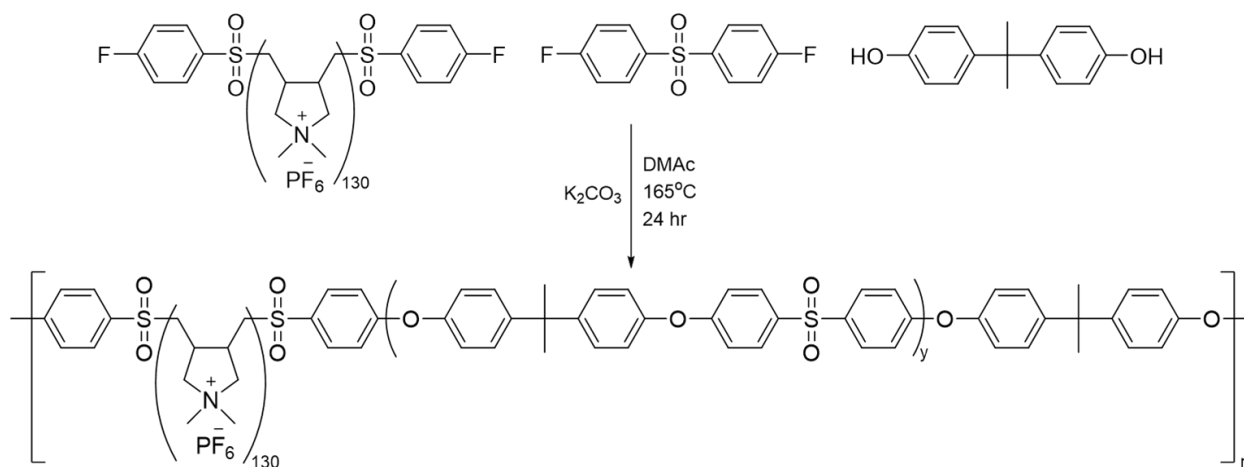


Figure 3.1 NMR spectrum of bis(4-fluorophenyl)sulfone difunctionalized PDADMA(PF₆).

3.4.2 Synthesis, Characterization, and Properties of Multiblock Polysulfones

The desired aromatic polysulfone was synthesized through the condensation reaction between bis(4-fluorophenyl)sulfone and deprotonated bisphenol A (Scheme 3.2). To produce multiblock copolymers, the appropriate stoichiometric amount of the small molecule difluoro monomer was replaced with the functionalized oligomer.



Scheme 3.2 Synthesis of PSf-PDADMA(PF₆) multiblock copolymers.

Because it is known that the composition of a block copolymer has a significant influence on the morphology and therefore properties of the material, copolymers were synthesized at approximately 20, 30, 40, and 50 wt. % PDADMA(PF₆) (Table 3.1). Good agreement between the monomer feed ratios and copolymer composition was determined by ¹H NMR spectroscopy in which the integration of the peaks from the methylene linkages of the DADMA(PF₆) repeat units was compared to the integration of the aromatic peaks resulting from the sulfone repeat units (Figure 3.2). All feed ratios successfully produced copolymers.

Table 3.1 Composition of the monomer feed, copolymer product, and yield for all multiblock copolymerizations.

Trial	Monomer feed		Copolymer product		Yield (mass %)
	Mole% DADMA(PF ₆)	Mass% DADMA(PF ₆)	Mole% DADMA(PF ₆)	Mass% DADMA(PF ₆)	
1	32	21	17	11	88
2	42	39	44	32	92
3	55	40	50	38	88
4	65	51	61	49	88

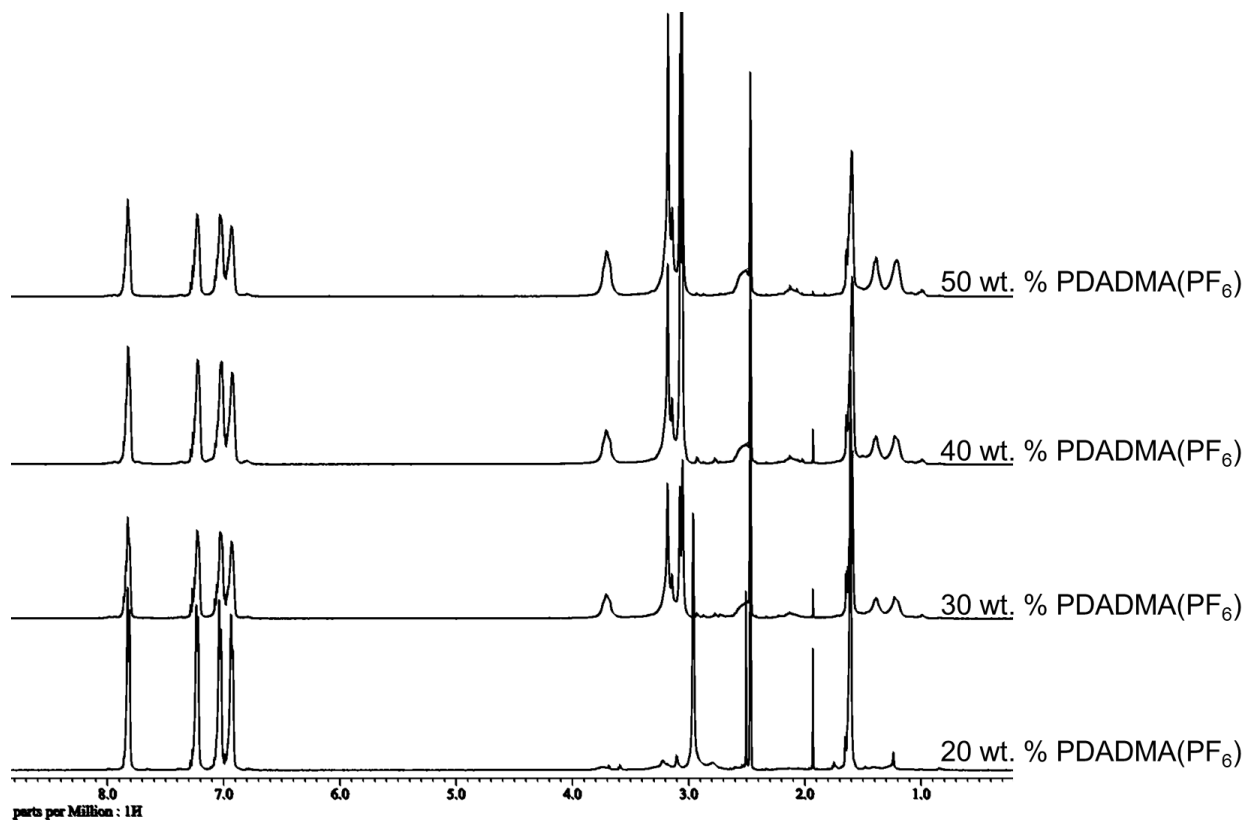


Figure 3.2 ^1H NMR spectra of all multiblock copolymers.

To produce polymer films, approximately 15 wt. % polymer solutions in DMAc were passed through syringe filters onto glass slides to cover the slide entirely. The solvent was evaporated slowly, and the free-standing films were delaminated by submerging the slides in DI water. While all copolymer compositions did form stand-alone films, the properties varied notably with PDADMA(PF₆) incorporation. While polysulfones are known to produce films and membranes with good strength and flexibility, homo-PDADMA(PF₆) forms very brittle films that cannot be readily handled. The discrepancy in properties meant the copolymers containing more PDADMA(PF₆), specifically 50 wt. %, were significantly more brittle and less flexible than those containing a greater amount of polysulfone. Despite some of the films possessing poorer properties, film-forming capacity is only accomplished in polymers of relatively high molecular weight. Because step-growth polymerizations are highly dependent on exact stoichiometric balance, the ability to produce high molecular weight polymer indicates that the PDADMA(PF₆) oligomers were both quantitatively functionalized and accurately characterized. Additionally, it was important to ensure that the inclusion of PDADMA(PF₆) blocks did not

detrimentally influence the thermal stability of the polysulfones. Even at the highest incorporation of PDADMA(PF₆), TGA showed no significant degradation of the copolymer until 283 °C. The 50 wt. % copolymer was also characterized to have a T_g of 182 °C. The decomposition temperature and T_g of homopolysulfone synthesized under the same conditions were found to be 448 °C and 188 °C, respectively. The PSf-PDADMA(PF₆) copolymers could be processed by melt pressing above their T_g, but the properties of the solvent cast films were superior to those made by melt pressing.

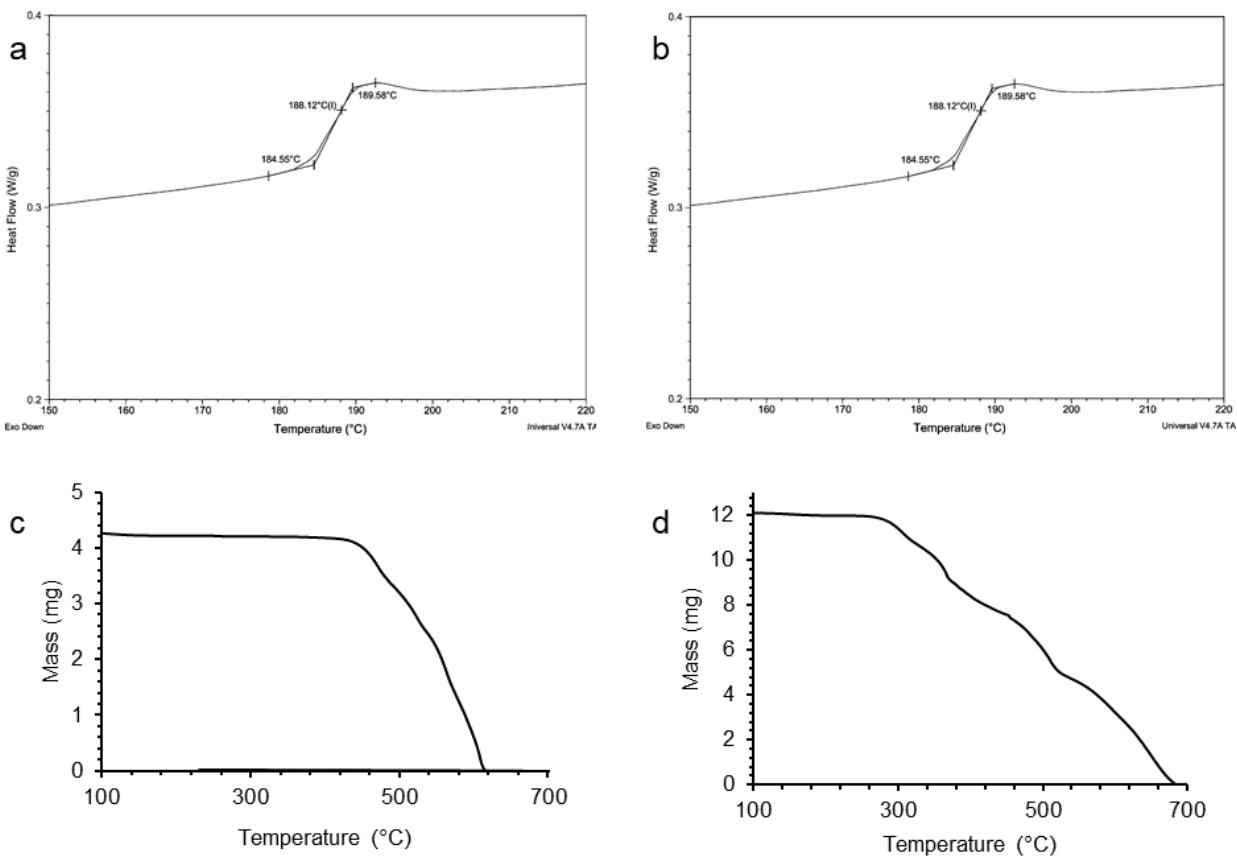


Figure 3.3 DSC curves showing T_g for the PSf homopolymer (a) and 50 wt. % PSf-PDADMA(PF₆) (b). TGA curves showing the decay temperatures of the PSf homopolymer (c) and 50 wt. % PSf-PDADMA(PF₆) (d).

3.4.3 Moisture-Swing, Direct-Air CO₂ Uptake Testing

For our membranes to be used as CO₂ capture materials, they needed to be converted from PF₆ counterions to hydroxide counterions. A modified version of a previous counterion exchange was used.⁸ The cast films were submerged in saturated potassium chloride solutions and refluxed for 96 hours. The films were then washed with DI water and patted dry with a Kim

Wipe before being transferred to a saturated potassium hydroxide solution for an additional 48 hours. Because the 50 wt. % PDADMA(PF₆) film was more brittle than the other compositions, it broke into a few large pieces during the refluxing step and no longer had the continuous surface area required for testing. The 20, 30, and 40 wt. % copolymers, anticipated to be in the hydroxide form, were mailed to Arizona State University for CO₂ uptake testing.

To perform the moisture-swing testing, the polymer films were dried, massed, and placed in a sample holder. The humidity level was changed by cycling the closed system air through a humidity controller. The humidity was cycled between 10 ppt (38 % relative humidity at 22 °C) and 25 ppt (96 % relative humidity at 22 °C). The concentration of CO₂ and water in the exhaust gas was measured in real time by an Li-Cor model Li-840A infrared gas analyzer (IRGA). For membranes demonstrating moisture-sensitive CO₂ uptake and release, the dry membranes should have a high affinity for CO₂ that is then released when relative humidity is high (Figure 3.4)

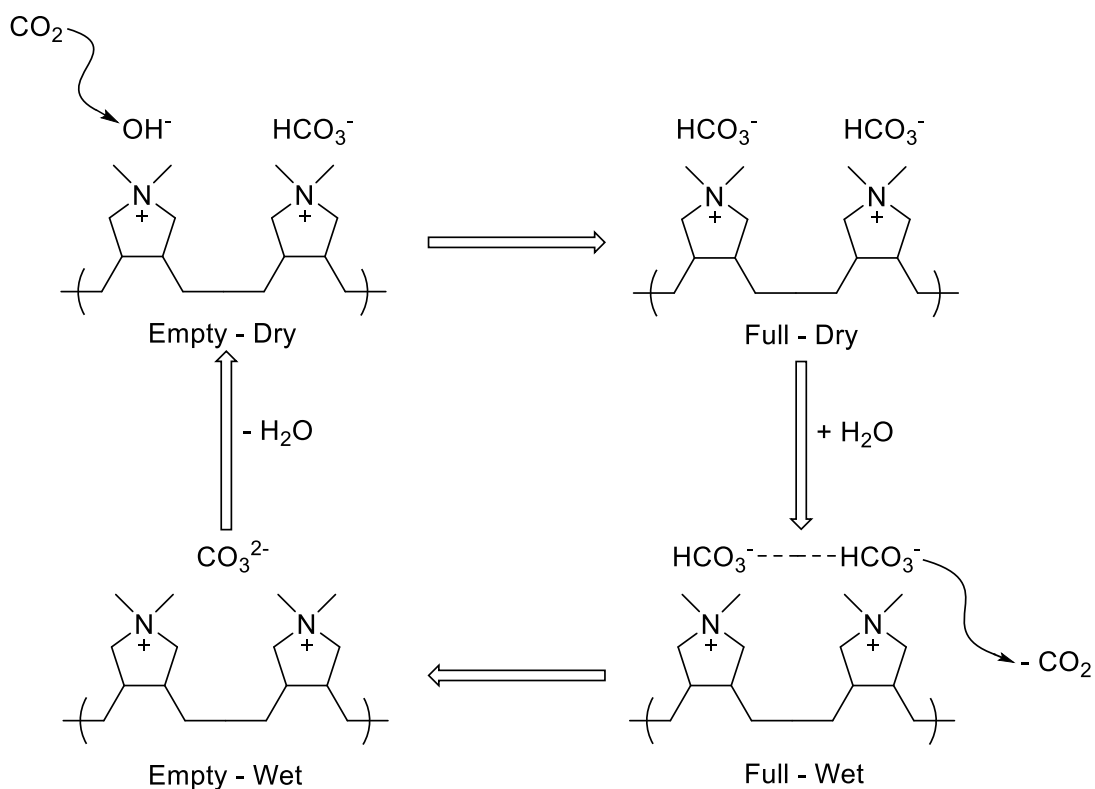


Figure 3.4 Schematic of the moisture-swing CO₂ uptake and release by PDADMA(OH) units.

For the 20 wt. % PDADMA(PF₆) film, the change in concentrations of CO₂ resulting from the moisture swing is not statistically above the baseline values (Figure 3.5 (a)). Therefore, the 20 wt. % film does not appear to be suitable as a membrane for direct-air, moisture-swing

CO₂ capture. Both the 30 and 40 wt. % films demonstrate CO₂ concentration changes statistically different from a negative control, indicating these films have some CO₂ capture capacity (Figure 3.5 (b) and (c)). The 30 wt. % PDADMA(PF₆) film demonstrated average CO₂ uptake of approximately 15 μmol/g. The 40 wt. % PDADMA(PF₆) film demonstrated average CO₂ uptake of approximately 36 μmol/g. As was anticipated, the film containing a higher concentration of ammonium groups had an increased affinity for CO₂.

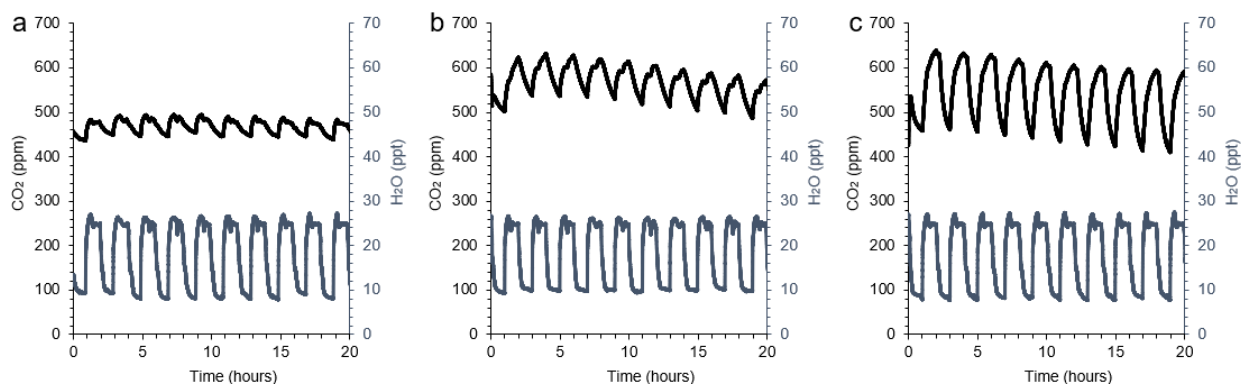


Figure 3.5 Changes in CO₂ concentration in parts per million (black) and relative humidity in parts per thousand of H₂O (grey) for the 20 (a), 30 (b), and 40 (c) wt. % copolymer films.

Though the multiblock copolymers do have the capacity for both the uptake and release of CO₂ as a function of relative humidity, the total concentrations absorbed were orders of magnitude lower than would be necessary for the materials to be viable at a large scale. Although there may be many reasons for this less than desirable performance, one main factor to consider is total hydroxide ion concentration. In this system, CO₂ uptake requires the presence of hydroxide or bicarbonate counterions when the membrane is in the wet stage. Because of the properties of the polysulfone blocks, film-forming copolymers were produced at relatively high cation concentrations, but the material properties of the membranes worsen with increasing concentrations of the ammonium block. Therefore, the CO₂ uptake capacity and membrane strength and flexibility are conflicting properties.

In addition to the influence of ammonium concentration on CO₂ affinity, the effectiveness of the ion exchange to hydroxide is also crucial for this application. Since PF₆ does not react with CO₂, any residual PF₆ counterions will decrease the CO₂ uptake capacity of the polymer membranes. After moisture-swing testing indicated a lower-than-expected CO₂ uptake for the multiblock polysulfones, we questioned the effectiveness of the counterion exchange. Upon FT-IR analysis of the supposedly ion exchanged membranes, it was discovered that a large

characteristic PF₆ peak was still present. While the counterion exchange procedure was previously demonstrated to be effective for diallylpiperidinium polymers,⁸ the reduced steric hinderance of the ammonium unit in DADMA(PF₆) may result in higher affinity for the counterion. To realize the full potential of these membranes for CO₂ uptake, an effective procedure for quantitative counterion exchange must be developed. An additional option is the determination of reaction conditions that allow functionalized oligomers to be used in the chloride form, but the solubility of DADMAC and its hygroscopic behavior may be problematic during the synthesis of polysulfones. Despite these challenges, the initial demonstration of CO₂ affinity and unique properties of PSf-PDADMA multiblock copolymers maintain their position as interesting materials for further investigation.

3.5 Conclusions

A synthesis method was developed to produce multiblock copolymers containing polysulfone and polydiallyldimethylammonium blocks. Bis(4-fluorophenyl)disulfide was demonstrated to effectively make fluorophenyl capped oligomers as a photoiniferter. Oxidation to fluorophenylsulfone end-groups followed by counterion exchange to PF₆ was shown to produce a form of the oligomers which could be incorporated into multiblock polysulfones via an in-situ reaction. The copolymerization method was found to be effective for the production of multiblock copolymers at a variety of compositions, all of which demonstrated film forming capacity, with those of higher polysulfone content producing films with good strength and flexibility. The high yield, good agreement between monomer feeds and copolymer compositions, and good material properties of the copolymers indicated that the iniferter-based synthesis was an effective technique to produce high molecular weight polymer. The permanent positive charges and good strength and stability of the multiblock polysulfones resulted in materials of interest for moisture-swing, direct-air CO₂ capture. Assessment of the copolymer films for CO₂ uptake, after an attempt to counterion exchange from PF₆ to hydroxide, showed that some of the films demonstrated reversible CO₂ absorption. However, the total CO₂ uptake observed was significantly lower than necessary for commercially viable materials. The preliminary results indicate incomplete counterion exchange may have occurred and that a more effective ion exchange procedure could increase the performance of this unique class of materials.

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CHAPTER 4
SYNTHESIS AND PROPERTIES OF CATIONIC MULTIBLOCK POLYARAMIDES AND
POLYIMIDES

Alison Biery¹ and Daniel Knauss¹

4.1 Abstract

Polydiallyldimethylammonium chloride (PDADMAC) is a useful material due to its high charge density and alkaline stability, but its hydrophilic nature limits applications to those where the dissolved polymer is appropriate. To make polymers suitable for applications as films and membranes containing the diallyldimethylammonium moiety, multiblock copolymers of polyaramides and polyimides, materials known for their excellent physical properties and stabilities, were synthesized. Aminophenyl difunctionalized PDADMAC oligomers were synthesized using a disulfide iniferter then counterion exchanged to the hexafluorophosphate anion to produce telechelic oligomers with good solubility in polar aprotic solvents. The oligomers were reacted in-situ with the proper difunctional monomers to produce polyaramides, polyetheraramides, polyimides, and polyetherimides. All the classes of copolymers were synthesized over a range of compositions at high yield and material properties were demonstrated to be a result of both the backbone chemistry and the composition. Several of the synthesized copolymers formed films with good clarity, strength, and flexibility. The copolymers containing ether linkages had increased backbone flexibility and demonstrated better film-forming properties. The multiblock copolyaramides and copolyimides demonstrate a method to produce materials with excellent thermal stability and good strength and flexibility, making them uniquely capable of serving as water insoluble, cationic films and membranes.

4.2 Introduction

Cationic polyelectrolytes are increasingly important materials with applications including anion exchange membranes,^{1,2} antibacterial coatings,^{3,4} gene delivery systems,^{5,6} and water purification.^{7,8} While many cationic groups can be incorporated into polymeric materials,

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quaternary ammonium groups are the most widely used due to their high charge density, material tunability, and chemical and thermal stability.^{9,10} A variety of synthetic techniques can be used to incorporate ammonium groups into polymers. When quaternary ammonium monomers are employed, formal cationic groups are integrated directly into the polymer backbone.

Diallyldimethylammonium chloride (DADMAC) is an interesting quaternary ammonium monomer because it undergoes cyclopolymerization, a unique radical polymerization mechanism that produces linear polymer backbones composed of enchainned pyrrolidinium units.¹¹ The homopolymer, PDADMAC, is known for particularly high charge density and alkaline stability that results from the steric hindrance of the cyclized ammonium group to nucleophilic attack.¹²

Since its discovery, PDADMAC has become an industrially important polymer.¹³ To expand the possible structures and properties of DADMAC containing materials, the monomer has been incorporated into a variety of copolymers. Copolymerization has overcome the often-limited molecular weight of homo-PDADMAC and incorporated new functional groups in the polymer backbone to improve the properties of these materials for specific applications.¹⁴ However, the hydrophilic nature of DADMAC and the inherent difficulty of copolymerizing comonomers with very different solubilities means that most reported copolymers of DADMAC are with other water-soluble monomers.¹⁵ Therefore, the possible applications of DADMAC containing polymers are significantly limited to areas where water-soluble polymers are suitable. The incorporation of diallyldimethylammonium groups into water-insoluble polymers could produce an interesting class of materials which can act as charged, base-stable films and membranes.

Polyaramides and polyimides are two significant classes of materials known for their strength and stability.^{16,17} Due to the good material properties and hydrophobicity of these polymers, they are used for a wide range of applications in the form of films and membranes.¹⁸⁻²⁰ Incorporating aramide and imide functionalities into DADMAC copolymers should produce materials with good properties and stabilities. However, there are synthetic challenges that must be overcome to produce copolymers containing these very different materials. In addition to solubility differences, the radical polymerization mechanism through which DADMAC is synthesized is incompatible with the step-growth polymerizations used to make polyimides and polyaramides.

Iniferters are functionalized reagents that act as radical initiators, chain transfer agents, and terminators.²¹ When iniferters are effectively employed in radical polymerizations, the resulting materials are telechelic oligomers of controllable molecular weight and end-group functionality. When end-groups are properly selected, the radically synthesized difunctional oligomers can be incorporated into step-growth polymerizations through the same reactivity as conventional difunctional monomers.²² The use of an aminophenyl disulfide iniferter during radical DADMAC polymerization was proposed in this research to produce telechelic PDADMAC oligomers with amine functionality. It has been demonstrated that the DADMAC monomer and PDADMAC polymer can be made water-insoluble through the ion exchange of chloride to the hydrophobic anion hexafluorophosphate (PF₆).²³ When the functionalized PDADMAC oligomers are converted to the PF₆ form, the resulting telechelics are not only water insoluble, but soluble in a variety of high-boiling, polar, aprotic solvents. Therefore, the ion-exchanged PDADMA(PF₆) oligomers are fully suitable for the incorporation into step-growth polymerization reactions. The amine-capped oligomers were reacted in the proper stoichiometries with diamine and either diacid (polyaramide) or dianhydride (polyimide) monomers in-situ to make multiblock copolymers. The objective of this work was to produce copolymers with both cationic functional groups and good material properties. Materials were synthesized to study how both polymer chemistry and composition would influence the resulting properties.

4.3 Experimental

4.3.1 Materials

DADMAC was obtained as an aqueous solution from TCI America and was determined by Mohr titration to be 70 % DADMAC by weight. KPF₆ (98 %) was used without further purification from Aldrich. 4-Aminothiophenol (97 %) and TEMPO (98 %) were used as received from Aldrich. Formic acid (88 %) from Fisher Scientific and acetic anhydride (99 %) Sigma-Aldrich were used as received. Isophthalic acid (IPA) (99 %) was received from Aldrich and recrystallized twice from ethanol. *M*-phenylenediamine (mPDA) (99 %) was purchased from Aldrich, recrystallized twice from diethyl ether, and stored in an amber bottle in the freezer. Oxydianiline (ODA) (97 %) was obtained from Aldrich and twice sublimed. Triphenylphosphite (TPP) (97 %) was obtained from Aldrich and was dissolved in diethyl ether; washed with 5 % NaOH, DI water, and saturated NaCl; dried with Na₂SO₄, and the ether evaporated. Pyridine

(99.8 %) was purchased from Sigma-Aldrich and fractionally distilled from KOH. LiCl (99.5 %) was used as received from Fisher Scientific. Pyromellitic dianhydride (PDA) (97 %) was obtained from Aldrich and twice sublimed. Bisphenol A dianhydride (BPADA) (95 %) was purchased from Oakwood Chemical and twice recrystallized from toluene with a small amount of acetic anhydride. NMP (99 %) was received from Sigma-Aldrich and fractionally distilled from a toluene azeotrope. DMAc (99 %) was purchased from Thermo Scientific and distilled from calcium oxide under nitrogen. All solids were dried under vacuum overnight before use. All other reagents were used as received from commercial sources. A model number SCT-4 UV pen lamp (25 amps, 115 volts) was obtained from Ultra-Violet Products, Inc.

4.3.2 Characterization

Molecular structure, product purity, and copolymer composition were determined by ^1H NMR spectroscopy performed on a JEOL ECA-500 FT-NMR using deuterium oxide or DMSO- d_6 . Chemical shifts were referenced to residual solvent peak shifts. Infrared spectroscopy was performed on a Nicolet 4700 FT-IR. Background spectra were collected in open air and all sample spectra were performed on the appropriate polymer in the film form.

Imidization temperature and polymer decomposition temperatures were determined by thermogravimetric analysis (TGA), which was carried out on a Seiko Instruments TG/DTA 320. Samples were heated under air to 100 °C at 40 °C per minute, held at 100 °C for 5 to 10 minutes, then heated to 800 °C at 10 °C per minute before being cooled to room temperature. All runs were performed in a platinum pan with an empty platinum pan as reference. Differential scanning calorimetry (DSC) was performed on a TA Instruments Q20 DSC to measure thermal transitions. Samples in sealed T-zero aluminum pans were heated from 0 °C to an appropriate maximum temperature between 230 °C and 300 °C at a rate of 10 °C per minute then cooled back down to 0 °C. Two cycles were completed and data from the second cycle was used to determine glass transition temperatures. All runs were completed under a 20 mL/min flow of N_2 with an empty T-zero aluminum pan as reference.

Atomic force microscopy (AFM) was performed on a Digital Instruments AFM Dimension 3100 in tapping mode using a 48 N m^{-1} silicone SPM-Sensor Pointprobe® tip. Films were prepared for AFM analysis by drop casting approximately 1 wt. % solutions of the polyetheraramide PEA-PDADMA(PF_6) films in DMAc or polyetherimide PEI-PDADMA(PF_6) in NMP on clean silicon wafers. The NMP was evaporated from the PEA copolymers under

nitrogen to limit the precipitation of polymer chains that can occur as the casting solution becomes more concentrated. The films equilibrated to ambient temperature and humidity before AFM analysis. The amplitude set-point ratio was 0.5 and the driving amplitude was 1 V.

4.3.3 Synthesis and Formamide Protection of Bis(4-aminophenyl)disulfide

A 250 mL round bottom flask with stir bar was charged with 4-aminothiophenol (4.915 g, 39.26 mmol), TEMPO (0.3177 g, 2.033 mmol), and acetonitrile (160 mL) then septum sealed. The clear yellow solution was sparged with oxygen for 30 minutes then heated to 60 °C for five hours. The now amber solution was cooled to room temperature and opened to air. Acetonitrile was removed by rotary evaporation to produce a viscous dark-brown liquid which solidified into brown, needle-like crystals after sitting overnight. The total solid product (4.1332 g) was transferred to a 50 mL round bottom flask and dissolved in formic acid (42 mL). Acetic anhydride (14 mL) was added dropwise via addition funnel over 30 minutes. The reaction proceeded at room temperature for one hour before being quenched through the slow addition of DI water until no further light brown precipitate formed. The formamide product (bis(4-formamidophenyl)disulfide) was collected by vacuum filtration and washed with DI water until a neutral pH was obtained. The light brown powder was dried under vacuum (4.9735 g, 83 % yield). ¹H NMR (500 MHz, CDCl₃, δ): 7.45 (m, 4H, Ar H), 7.02 (m, 4H, Ar H).

4.3.4 Synthesis and Deprotection of Telechelic PDADMA(PF₆) Oligomers

To produce oligomers for use in the polyaramide synthesis, aqueous DADMAC solution (28.88 g, 125.0 mmol DADMAC) was diluted to 50 mL with methanol. This solution was transferred to a quartz test tube with 0.7609 g of bis(4-formamidophenyl)disulfide (0.7609 g, 2.500 mmol). The test tube was septum sealed and the clear, brown solution was sparged with nitrogen for 20 minutes in an ice bath. The solution was transferred to a 70 °C DI water bath for ten minutes to temperature equilibrate before being exposed to 254 nm UV irradiation from a pen lamp. After 24 hours, the solution was cooled to room temperature, opened to air, and solvent was removed by rotary evaporation. The resulting brown solid was dissolved in a minimal amount of methanol and precipitated in acetone. The precipitate was collected by vacuum filtration and dried before being transferred to a 100 mL round bottom flask with NaOH (1.67 g, 4.17 mmol) and DI water (80 mL). The alkaline solution was refluxed for 18 hours then most of the solvent was removed by rotary evaporation to produce a highly concentrated

solution. A small aliquot was taken for analysis and the remainder was precipitated into saturated KPF_6 solution. The tan solid was isolated by vacuum filtration, washed with excess DI water, and dried under vacuum (11.3 g, 32 % yield). NMR indicated the oligomer contained 33 repeat units ($9,198 \text{ g mol}^{-1}$). ^1H NMR (500 MHz, $\text{DMSO-}d_6$, δ): 7.10 (d, 4H; Ar H), 6.50 (d, 4H; Ar H), 5.37 (bs, 2H; CH_2), 3.57 (bs, 4H; CH_2), 3.11 (m, 6H; CH_3), 2.47 (bs, 2H; CH), 1.13 (m, 4H; CH_2).

Oligomer for use in the synthesis of soluble polyimides was synthesized following the above procedure but using 28.85 g of DADMAC solution and 0.7605 g of bis(4-formamidophenyl)disulfide. NMR spectroscopy indicated the oligomer contained 36 repeat units ($10,011 \text{ g mol}^{-1}$).

4.3.5 Synthesis of Multiblock *Meta*-Polyaramides (PA-PDADMA(PF_6))

Copolymers were synthesized to target a variety of block compositions from 20 to 50 % PDADMA(PF_6) by weight in the monomer feed. A representative procedure is as follows: a 50 mL oval-shaped round bottom flask with stir bar was charged with IPA (0.664 g, 4.000 mmol), mPDA (0.4240 g, 3.921 mmol), PDADMA(PF_6) oligomer (0.7300 g, 0.07937 mmol amine end-groups), and LiCl (0.909 g). The flask was septum sealed and sparged with N_2 for 30 minutes. NMP (14.0 mL), pyridine (4.5 mL), and TPP (4.6 mL, 15.4 mmol) were added by syringe transfer. The cloudy, light-yellow solution was sparged for an additional five to ten minutes then lowered into a 105 °C oil bath. After 24 hours, the solution was cooled to room temperature, opened to air, and poured slowly into stirring methanol. The resulting off-white solid was collected by vacuum filtration then redissolved in NMP and reprecipitated in methanol. The solid product was again collected by vacuum filtration, washed with methanol, and dried under vacuum (1.77 g, 97 % yield). Homopolymer was synthesized under the same conditions but without the inclusion of PDADMA(PF_6) oligomer.

4.3.6 Synthesis of Multiblock Polyetheraramides (PEA-PDADMA(PF_6))

Copolymers were synthesized to target a variety of block compositions from 20 to 50 % PDADMA(PF_6) by weight in the monomer feed. A representative procedure is as follows: a 50 mL oval-shaped round bottom flask with stir bar was charged with IPA (0.4154 g, 2.500 mmol), ODA (0.4873 g, 2.434 mmol), PDADMA(PF_6) oligomer (0.6100 g, 0.06632 mmol amine end-groups), and LiCl (0.757 g). The flask was septum sealed and sparged with N_2 for 30 minutes.

NMP (17.0 mL), pyridine (5.7 mL), and TPP (1.4 mL, 5.5 mmol) were added by syringe transfer. The cloudy, light-yellow solution was sparged for an additional five to ten minutes then lowered into a 105 °C oil bath. After 24 hours, the solution was cooled to room temperature, opened to air, and poured slowly into stirring methanol. The resulting white solid was collected by vacuum filtration and redissolved in NMP and reprecipitated in methanol. The solid product was again collected by vacuum filtration, washed with methanol, and dried under vacuum (1.42 g, 94 % yield). Homopolymer was synthesized under the same conditions but without the inclusion of PDADMA(PF₆) oligomer.

4.3.7 Synthesis of Multiblock Polyimides (PI-PDADMA(PF₆))

Copolymers were synthesized to target a variety of block compositions from 20 to 50 % PDADMA(PF₆) by weight in the monomer feed. A representative procedure is as follows: A 25 mL, two neck, round bottom flask with stir bar was charged with ODA (0.3373 g, 1.415 mmol), PDADMA(PF₆) oligomer (0.4800 g, 0.08494 mmol amine end-groups), and DMAc (5 mL). The solid was dissolved to produce a yellow solution. This was placed in an ice bath and PMDA (0.3817 g, 1.500 mmol) was added in small portions over 30 minutes followed by a final 2 mL of DMAc. The solution was allowed to warm slowly from 0 °C to room temperature overnight. After 16 hours, the solution was opened to air and diluted with approximately 2 mL of DMAc before being poured slowly into DI water. The product was collected, redissolved in DMAc, reprecipitated into DI water, collected by vacuum filtration, and dried under vacuum at room temperature to produce the polyamic acid as a powdery yellow solid (1.24 g, 156 % yield).

Films of the poly(amic acid) were cast from DMAc then heated slowly to approximately 220 °C to imidize with the release of water. Conversion to the imide was confirmed by lack of solubility in polar aprotic solvents and disappearance of the carboxylic acid peak in IR. Homopolymer was synthesized under the same conditions but without the inclusion of PDADMA(PF₆) oligomer.

4.3.8 Synthesis of Multiblock Polyetherimides (PEI-PDADMA(PF₆))

Copolymers were synthesized to target a variety of block compositions from 20 to 50 % PDADMA(PF₆) by weight in the monomer feed. A representative procedure is as follows: An addition funnel was charged with 0.4424 g (0.8500 mmol) BPADA and 2.5 mL of NMP then swirled until most of the solid had dissolved. A 25 mL, two neck, round bottom flask was

charged with 0.1621 g (0.8095 mmol) ODA, 0.4050 g (0.0404 mmol) PDADMA(PF₆), and 2.5 mL NMP. This was stirred until all solid had dissolved to produce a yellow solution. The BPADA solution was added slowly to the flask over 30 minutes followed by a rinse of the addition funnel with 1 mL of NMP to produce a viscous, somewhat lighter yellow solution.

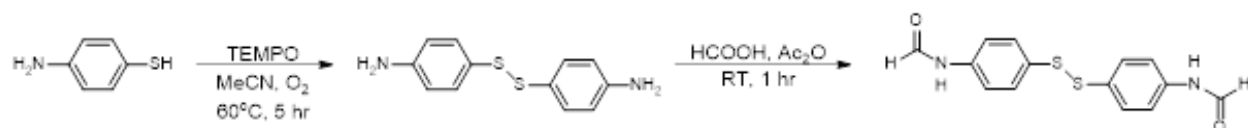
After 16 hours at room temperature, imidization was carried out in-situ. Toluene (3 mL) and quinoline (0.15 mL, 1.28 mmol) were added to the reaction mixture. The flask was connected to a Dean-Stark trap prefilled with toluene and a water-cooled condenser. The solution was heated in an oil bath from room temperature to 180 °C over one hour then held at 180 °C for six hours. At approximately five hours, the Dean-Stark trap was emptied to remove the remaining toluene. After the total 25 hours of reaction time, the viscous brown solution was cooled to room temperature, opened to air, diluted with an additional 1 mL of NMP, and precipitated into stirring methanol. The polymer product was twice redissolved in NMP and reprecipitated in methanol to produce an off-white solid (0.95 g, 94 % yield). Homopolymer was synthesized under the same conditions but without the inclusion of PDADMA(PF₆) oligomer.

4.4 Results and Discussion

4.4.1 Synthesis of Functionalized PDADMA(PF₆) Oligomers

4.4.1.1 Iniferter Synthesis

To produce amine functionalized oligomers, a properly functionalized disulfide iniferter was used. Bis(4-aminophenyl)disulfide was synthesized through the (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) catalyzed oxidation of 4-aminothiophenol (Scheme 4.1). However, aromatic amines are known retarders for radical reactions,^{24,25} and preliminary experiments determined that the amine iniferters were not suitable for oligomerization. Through a reversible protection reaction, the primary amine groups were converted to formamide groups to produce bis(4-formamidophenyl)disulfide (Scheme 4.1). Quantitative protection was determined through the analysis of peaks present in the aromatic region of the ¹H NMR spectrum.



Scheme 4.1 Synthesis of formamide protected disulfide iniferter.

4.4.1.2 Synthesis of PDADMA(PF₆) Blocks

Bis(4-formamidophenyl) disulfide functions as a photo-iniferter. When exposed to UV irradiation, the iniferter cleaves to produce two formamidophenyl sulfide radicals that initiate the polymerization of DADMAC. Because termination by recombination is favored in DADMAC polymerization,²⁶ there were two anticipated termination mechanisms in the polymerization of DADMAC using a disulfide iniferter: recombination of growing PDADMAC chains and chain transfer to the sulfide radical. Since both termination pathways lead to end-groups resulting from the iniferter molecule, it could be assumed that all oligomer chains were effectively difunctionalized.

To produce telechelic oligomers with the proper reactivity for incorporation into polyaramides (PA) and polyimides (PI), it was necessary to recover the protected amine functionality. The formamide group was deprotected to produce the primary amine through refluxing in a highly alkaline solution (Scheme 4.2), a procedure that took advantage of the base stability of PDADMAC. The deprotection of the oligomers was characterized by shifting peaks in the aromatic region of the ¹H NMR spectrum of the oligomer.

Quantitative ¹H NMR was also used to determine the average number of DADMAC repeat units, and therefore molecular weight, of the oligomers (Figure 4.1). The DADMAC repeat units result in four unique proton environments. For molecular weight determination, the area of the peaks from 0.7 ppm to 2.6 ppm, which correspond to the four protons of the chiral methylene linkages in the PDADMAC backbone, were compared to the average area of the two aromatic peaks resulting from the aromatic end-groups. NMR analysis was used to determine molecular weight of the cationic oligomers because the molecular weight characterization of polyelectrolytes through more conventional methods like chromatography, mass spectrometry, and viscometry is inherently difficult.²⁷⁻³¹ As a result, accurate molecular weight determination of the final charged multiblock copolymers was also not feasible. Two oligomerization trials were performed with a molar ratio of monomer to iniferter of 50:1. For the first and second trial the number of repeat units were determined to be 33 and 36 respectively (Figure A.1). The similarity of these two trials indicates that molecular weight can be controlled as a function of initiator and monomer concentrations. While the level of control achieved by these reactions is not as extensive as that possible with controlled radical polymerization techniques, iniferters are a facile way of achieving not only a general molecular weight but tunable functionalization.

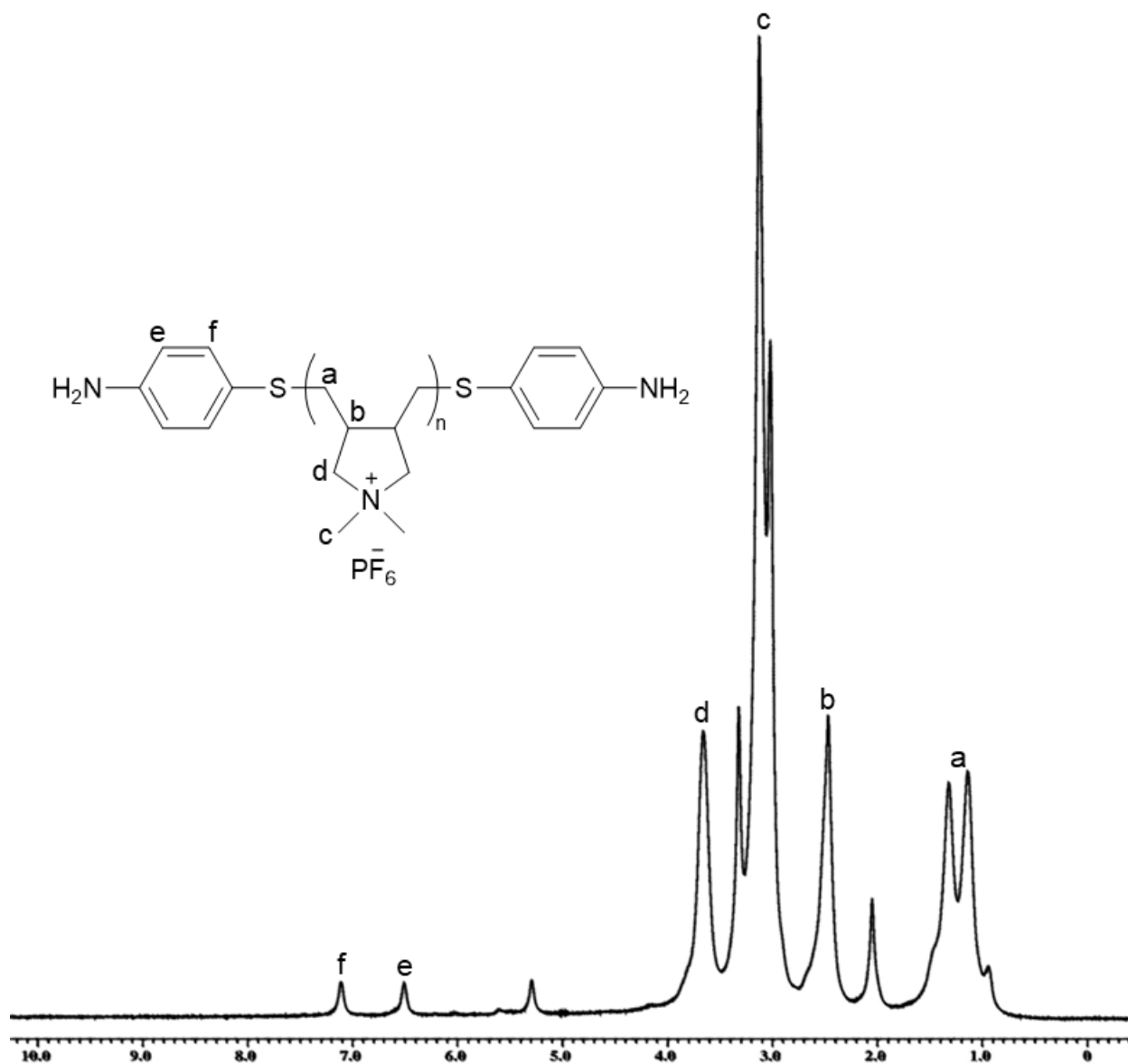
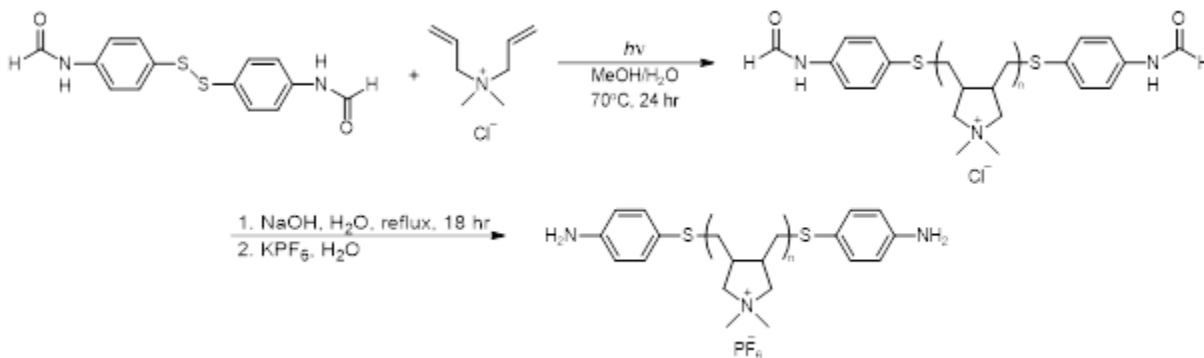


Figure 4.1 ^1H NMR spectrum of the 33 repeat unit, amine-functionalized PDADMA(PF_6) oligomer.

The amine-functionalized PDADMAC oligomers are highly soluble in water. However, polyaramide and polyimide syntheses are performed in high-boiling, polar, aprotic solvents like NMP and DMAc. To prepare telechelic oligomers with the proper solubility, the chloride counterions were exchanged for hexafluorophosphate. Ion exchange was characterized by the changing solubility and the appearance of a peak resulting from P-F bonds at 839 cm^{-1} in the FTIR spectrum (Figure A.2, Figure A.3). The resulting PDADMA(PF_6) oligomers were found to

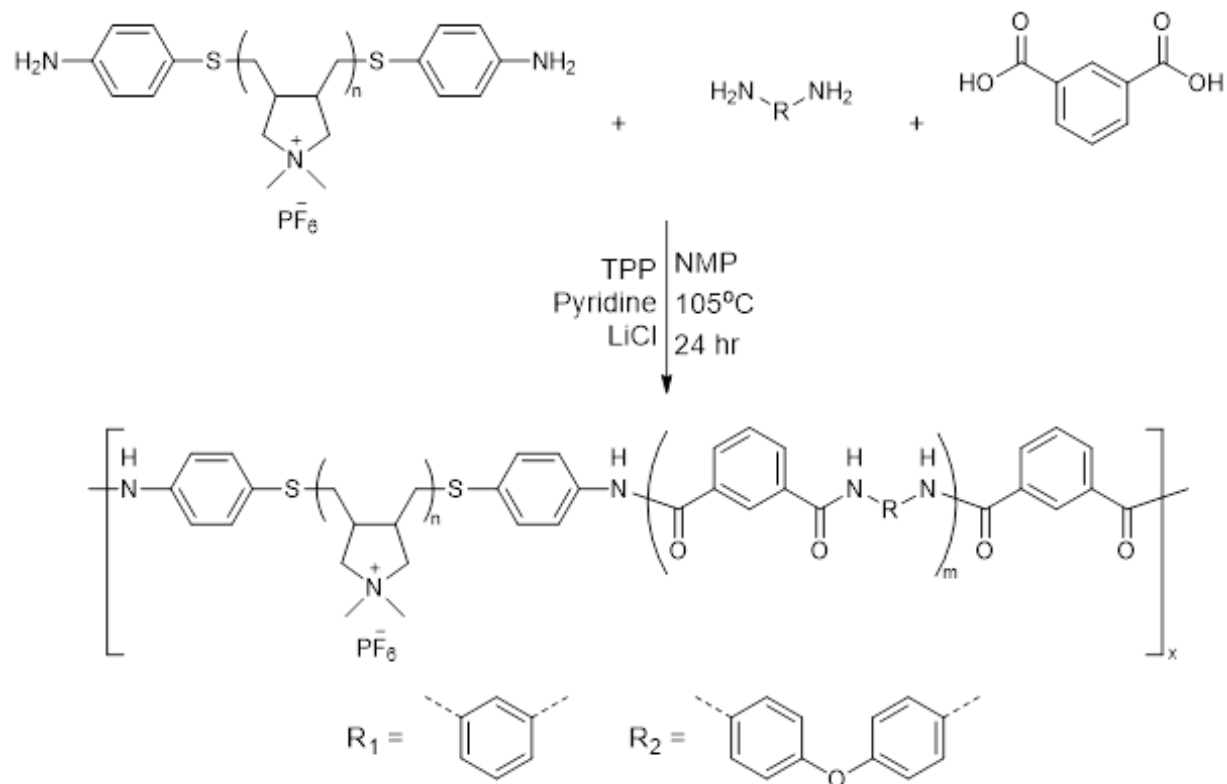
be insoluble in water and have high solubility in a variety of polar aprotic solvents, notably NMP and DMAc.



Scheme 4.2 Synthesis of end-functionalized PDADMA(PF₆) oligomers.

4.4.2 Synthesis and Film Properties of Multiblock Polyaramides

The amine-functionalized PDADMA(PF₆) blocks were incorporated into polyaramides via a Higashi-Yamazaki phosphorylation in which the diacid monomer forms a reactive salt intermediate with pyridine and triphenyl phosphate that promotes condensation with the diamine monomer (Scheme 4.3).³² The determination of suitable conditions for these polymerizations was previously reported.³³



Scheme 4.3 Synthesis of multiblock *meta*-polyaramides (R₁) and polyetheraramides (R₂).

The *meta*-linked polyaramide, commercially available as Nomex®, is known for its strength and thermal stability.³⁴ Because the properties of multiblock copolymers are dependent on their compositions, it was important to synthesize a variety of copolymer compositions.³⁵ Feed ratios of the PDADMA(PF₆) oligomers and difunctional monomers were chosen to produce copolymers of 20, 30, 40, and 50 wt. % DADMA(PF₆). For all ratios, good yields of polymer were obtained (Table 4.1). Copolymer compositions were quantified using ¹H NMR spectroscopy. Integration values of the amide peak at 10.6 ppm were compared to those of the DADMA(PF₆) repeat unit methylene linkages (Figure 4.2, Figures A.4-6). The excellent agreement between the oligomer/monomer feed ratios and final copolymer composition indicates that the PDADMA(PF₆) oligomers were incorporated into the block copolymers as expected and therefore must have been effectively difunctionalized. Both the 40 wt. % PA-PDADMA(PF₆) sample and synthesized homopolyaramide were determined to have T_gs above 240 °C (Figures A.7-8). The high T_g of the block copolymer material indicates that it maintained the excellent thermal properties for which the homopolymer is known. A separate T_g is not seen for the PDADMA(PF₆) block because thermal transitions in ionic polymers are often difficult to observe or characterize, leading to no consistent T_g data being available for diallyldimethylammonium polymers.³⁶⁻³⁹

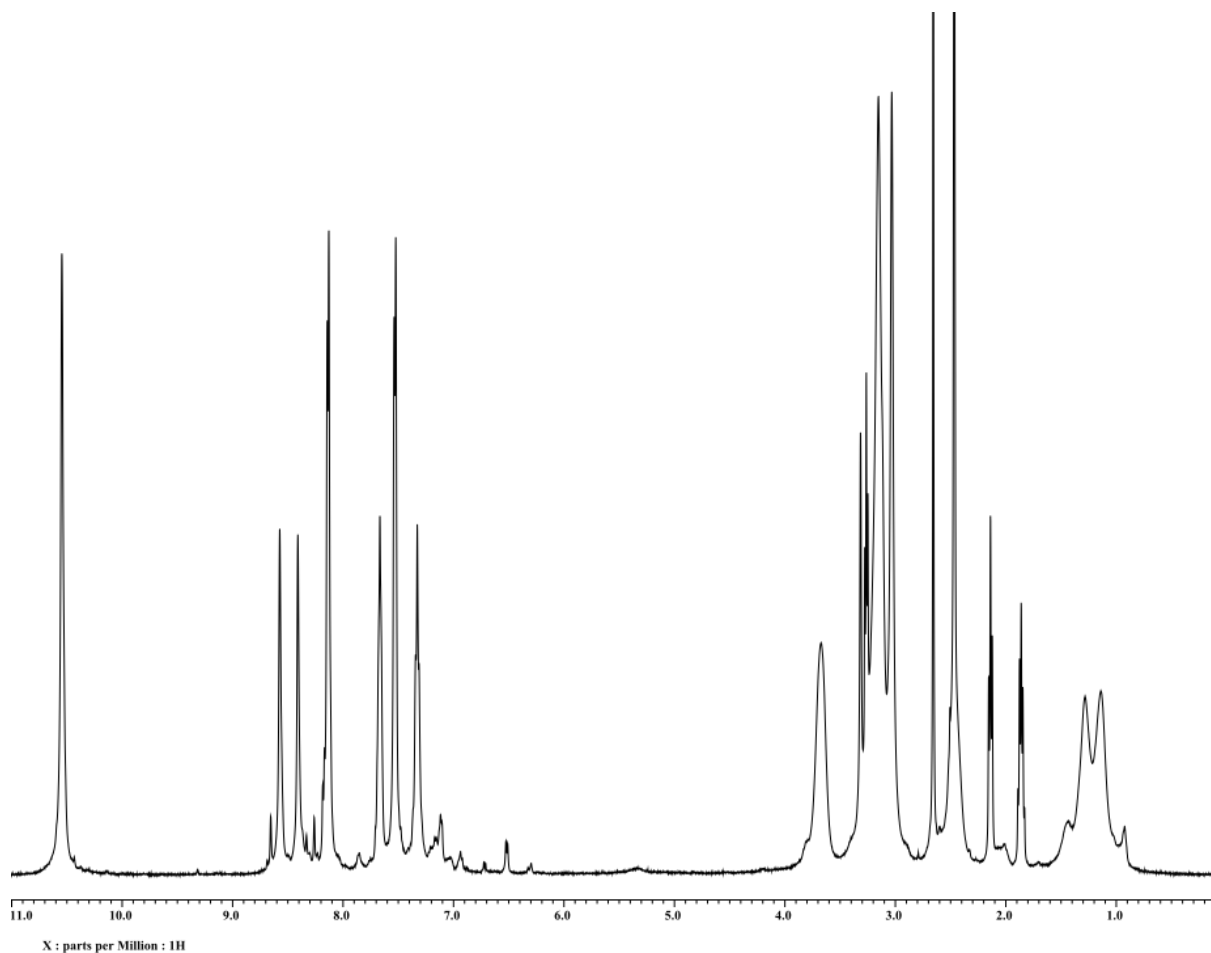


Figure 4.2 ^1H NMR spectrum of 50 wt. % PA-PDADMA(PF₆).

Table 4.1 Compositions of the monomer feeds and copolymer products and yields for the PA-PDADMA(PF₆) syntheses.

Trial	Monomer feed		Copolymer product		Yield [mass %]
	DADMA(PF ₆) [mole %]	DADMA(PF ₆) [mass %]	DADMA(PF ₆) [mole %]	DADMA(PF ₆) [mass %]	
1	20	22	16	18	86
2	30	33	27	30	93
3	40	43	31	36	97
4	50	53	47	51	93

To cast films, approximately 5 wt. % solutions of the PA-PDADMA(PF₆) polymers in DMAc were prepared. The solutions were filtered and drop cast on glass slides. After the solvent

was removed through gentle heating, the polymer films were delaminated by soaking the glass slide in DI water and examined qualitatively for their properties. A film of the homopolyaramide, prepared under the same reaction conditions but without the inclusion of PDADMA(PF₆) blocks, demonstrated reasonable flexibility. All the copolymer compositions could be cast as homogenous films, but the resulting properties were less than desirable. Higher concentrations of PDADMA(PF₆) led to noticeably weaker and more brittle films, which was as expected because homo-polyaramides have excellent physical properties, but homo-PDADMA(PF₆) does not form strong free-standing films. However, even at low PDADMA(PF₆) ratios, the resultant PA-PDADMA(PF₆) films were relatively weak and brittle. This may be a result of the very rigid backbone present in both homopolymers. To produce copolymers with improved film properties, we chose to increase the flexibility present in the polyaramide blocks.

Replacing the mPDA monomer with ODA produced polyetheraramides (PEAs) (Scheme 4.3), which are linked through the same reaction as the *meta*-polyaramides but contain a flexible ether linkage. The additional flexibility of the polymer backbone should decrease the molecular weight at which the polymer chains can entangle, thereby improving the properties of the polymer films. Using the same amine-capped PDADMA(PF₆) oligomers and Higashi-Yamazaki phosphorylation mechanism, PEA-PDADMA(PF₆) was synthesized in high yield at compositions of 20, 30, 40, and 50 wt. % DADMA(PF₆) (Table 4.2). Copolymer composition was determined by quantitative ¹H NMR spectroscopy (Figure 4.3, Figures A.9-11) using the same characteristic peaks of the etheraramide and DADMA(PF₆) repeat units.

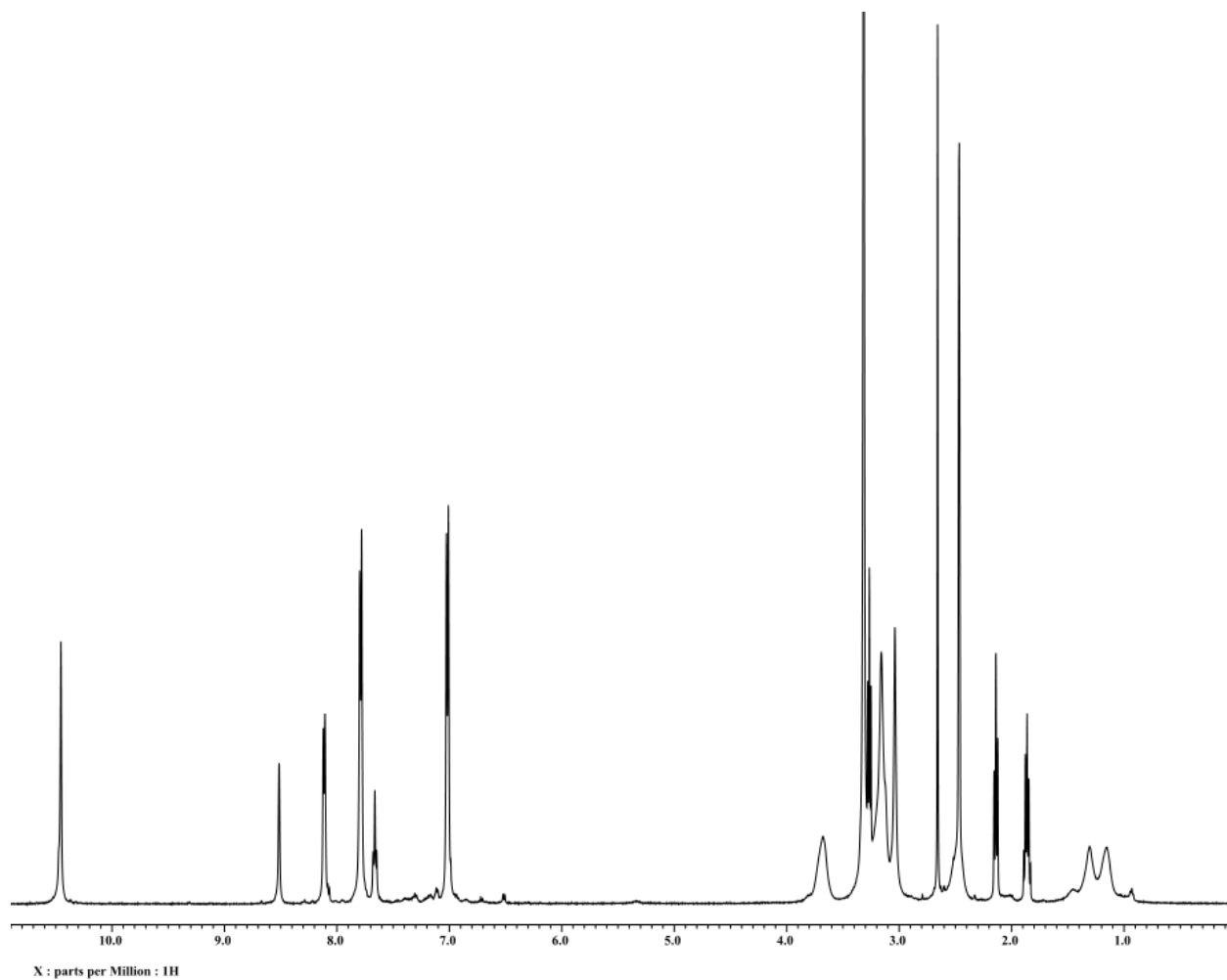


Figure 4.3 ^1H NMR spectrum of 50 wt. % PEA-PDADMA(PF₆).

Table 4.2 Compositions of the monomer feeds and copolymer products and yields for the PEA-PDADMA(PF₆) syntheses.

Trial	Monomer feed		Copolymer product		Yield [mass %]
	DADMA(PF ₆) [mole %]	DADMA(PF ₆) [mass %]	DADMA(PF ₆) [mole %]	DADMA(PF ₆) [mass %]	
1	25	20	20	17	86
2	37	30	33	29	87
3	47	40	43	38	94
4	57	50	57	52	85

As expected, the PEA-PDADMA copolymers had much better properties than the less flexible, *meta*-linked equivalents. While brittleness did increase with increasing PDADMA(PF₆)

incorporation, the 20, 30, and 40 wt. % compositions all formed flexible stand-alone films with good clarity and strength. The properties of these materials indicate that high molecular weight polymer was formed. To have reached high molecular weight in a step-growth polymerization, a sufficient functional group stoichiometry balance must have been achieved, meaning the PDADMA(PF₆) oligomers must have been quantitatively difunctionalized, effectively deprotected, and accurately characterized. DSC characterization of the 40 wt.% PEA-PDADMA(PF₆) sample and homopolyetheraramide demonstrated T_gs above 230 °C for both polymers. (Figures A.12-13). The properties of the PEA-PDADMA(PF₆) films makes these materials promising for membrane applications.

Tapping mode AFM was used to characterize the morphology of the cast PEA-PDADMA(PF₆) films. Light and dark domains in the resulting phase image (Figure 4.4) correspond to microphases enriched in the distinct polymer blocks. Clear phase separation can be seen for all compositions of the copolymers, though because the films were not annealed before analysis, no highly ordered phases were expected. Moving from the lower to higher incorporation of PDADMA(PF₆) appears to correspond to larger, more connected light domains. It can therefore be assumed that the microphase domains of the 20 wt. % PEA-PDADMA(PF₆) films are relatively small and disconnected. As the ratio of the two blocks becomes more equal, the domains become larger and more connected. It would be expected that this change in morphology would have an influence on the properties of the copolymer films.

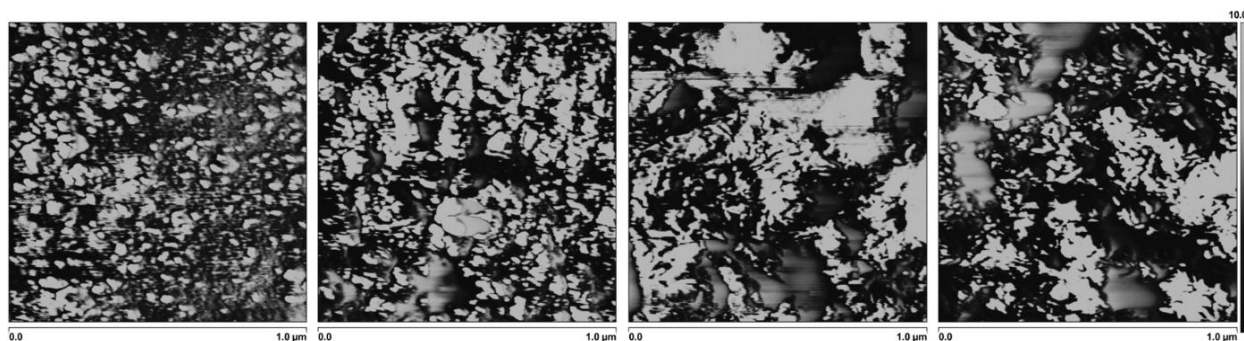
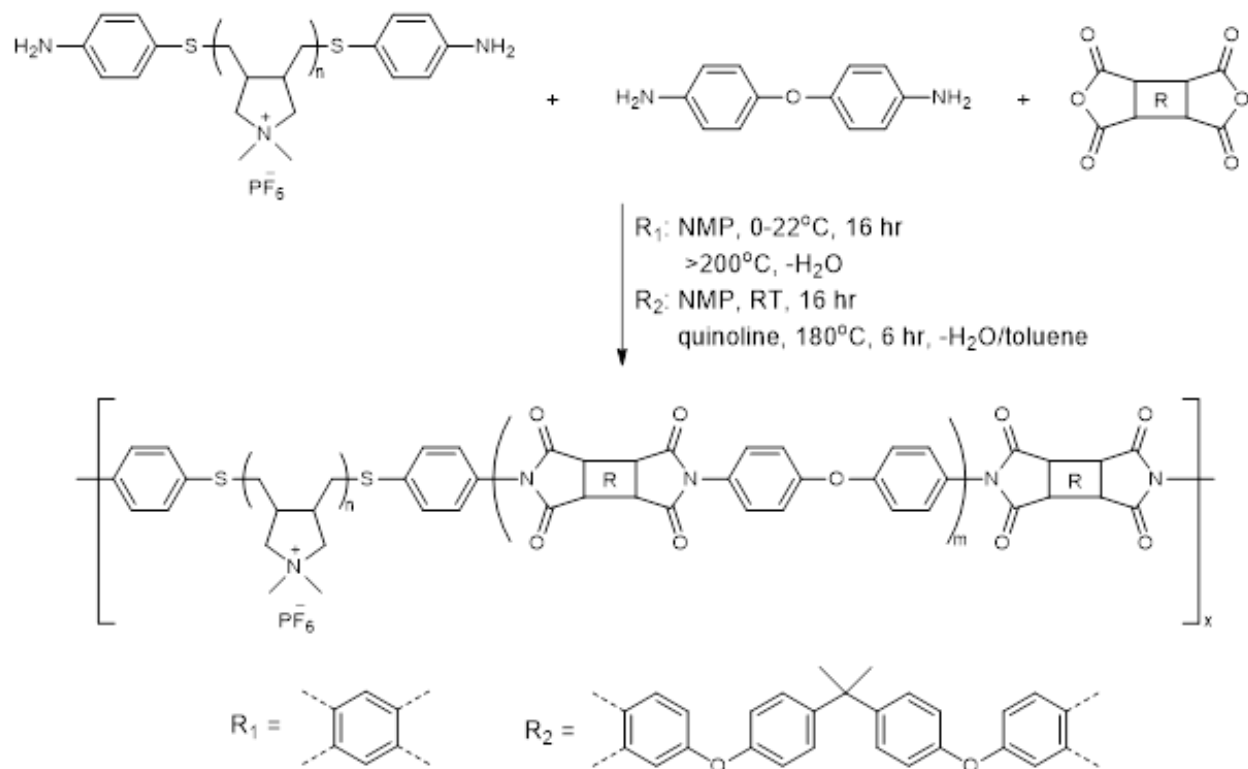


Figure 4.4 Tapping mode AFM phase images for the 20, 30, 40, and 50 wt. % PEA-PDADMA(PF₆) (left to right) copolymer films.

4.4.3 Synthesis and Film Properties of Multiblock Polyimides

Through an aminolysis reaction, the amine-functionalized oligomers were reacted with a diamine monomer and dianhydride monomer to produce multiblock poly(amic acid)s. The

poly(amic acid)s can be converted to polyimides by a ring-closing reaction with the removal of water (Scheme 4.4).



Scheme 4.4 Synthesis of multiblock polyimides (R_1) and polyetherimides (R_2).

PMDA and ODA were used as the dianhydride and diamine monomers to produce polyimides with structures analogous to the industrially important material Kapton.⁴⁰ To study the effect of copolymer compositions, monomer and oligomer feed ratios of 20, 30, 40, and 50 wt. % PDADMA(PF_6) were employed (Table 4.3). The resulting poly(amic acid)s were successfully synthesized for all feed ratios. Because imidization produces polymers that are insoluble in almost all solvents, isolation and characterization of the materials was done in the poly(amic acid) form. Quantitative ^1H NMR spectroscopy comparing the characteristic DADMA(PF_6) repeat unit peaks to the carboxylic acid peak at 10.6 ppm of the amic acid repeat units indicated excellent agreement between the monomer feed ratios and copolymer compositions (Figure 4.5, Figures A.14-16).

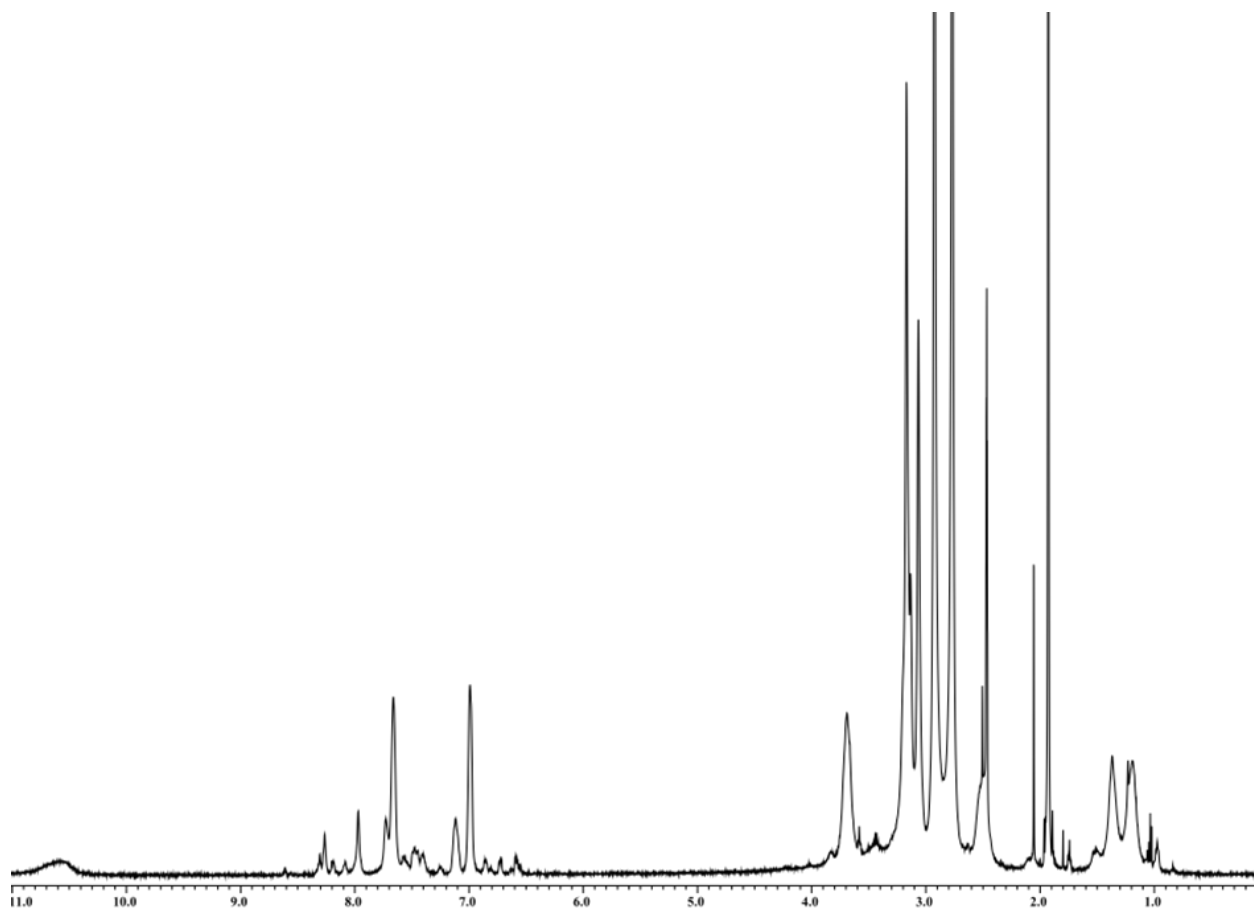


Figure 4.5 ^1H NMR spectrum of 50 wt. % PI-PDADMA(PF₆) in the poly(amic acid) form.

Table 4.3 Compositions of the monomer feeds and copolymer products (in poly(amic acid) form) and yields for the PI-PDADMA(PF₆) syntheses.

Trial	Monomer feed		Copolymer product		Yield [mass %]
	DADMA(PF ₆) [mole %]	DADMA(PF ₆) [mass %]	DADMA(PF ₆) [mole %]	DADMA(PF ₆) [mass %]	
1	27	20	21	15	98
2	39	30	36	26	105
3	49	40	53	42	156
4	60	50	65	55	100

Films of the polymers were cast from the soluble poly(amic acid) precursor by dropping a solution of approximately 5 wt. % polymer in NMP on a glass slide and heating gently to remove most solvent. TGA demonstrated that the imidization process, denoted by the loss of mass

corresponding to a loss of water, occurred at approximately 150 °C (Figure A.17). The poly(amic acid)s were therefore imidized by slowly heating the cast films to above 200 °C. Conversion to the imide was determined by the loss of solubility as well as the replacement of the carbonyl stretching peaks of the amide and carboxylic acid at 1712 and 1643 cm^{-1} respectively with a large carbonyl peak from the imide at 1706 cm^{-1} in FTIR spectra of the films.⁴¹ Once in the imide form, the PI-PDADMA(PF₆) films demonstrate no thermal transitions or decomposition through 280 °C, which is similar to that observed for the homopolyimide (Figure A.18).

All compositions of the multiblock poly(amic acid)s formed stand-alone films that could be converted to the polyimide. However, once in the imide form, the films were relatively strong but quite brittle. Furthermore, the amic acid functional groups are not stable in the presence of residual monomer or solvent. A reaction between the amide and carboxylic acid groups produces intermediates that can be converted back to the amic acid or to the imide. When an amide solvent like DMAc is present, these intermediates can instead undergo a cleavage reaction of the polymer backbone.⁴² Because the isolated polymers need to be dried at relatively low temperature to prevent unwanted imidization, which would make the material insoluble and difficult to work with, removing all residual solvent is challenging. The presence of a significant amount of residual solvent results in the reported yields above 100 % for the poly(amic acid)s (Table 4.3). As a result, the storage of the polymer materials in the amic acid form allows for slow decomposition and later film samples have noticeably worse properties than those cast shortly after synthesis. To improve the material properties of the polyimides and prevent degradation, soluble polyimides were synthesized.

The most relevant soluble polyimide is the polyetherimide (PEI) Ultem®, which takes advantage of the more flexible dianhydride, BPADA.¹⁷ The 9,800 g mol^{-1} amine functionalized oligomer was reacted in the proper stoichiometries with ODA and BPADA to produce 20, 30, 40, and 50 wt. % PDADMA(PF₆) multiblock copolymers (Scheme 4.3). The initial poly(amic acid) synthesis was performed in NMP at room temperature. Quinoline was added to the reaction mixture to serve as an imidization accelerator,⁴³ allowing the conversion to imide to occur at lower temperatures, and the reaction was heated to 180 °C with the removal of water as a toluene azeotrope to produce PEI-PDADMA(PF₆). Copolymer compositions were determined by integrating the characteristic DADMA(PF₆) peaks and comparing values to those of the methyl proton peaks from the BPA-type linkages (Figure 4.6, Figures A.19-21). Once again, good

agreement was seen between the monomer feed and copolymer compositions, indicating the oligomer synthesis was reproducible.

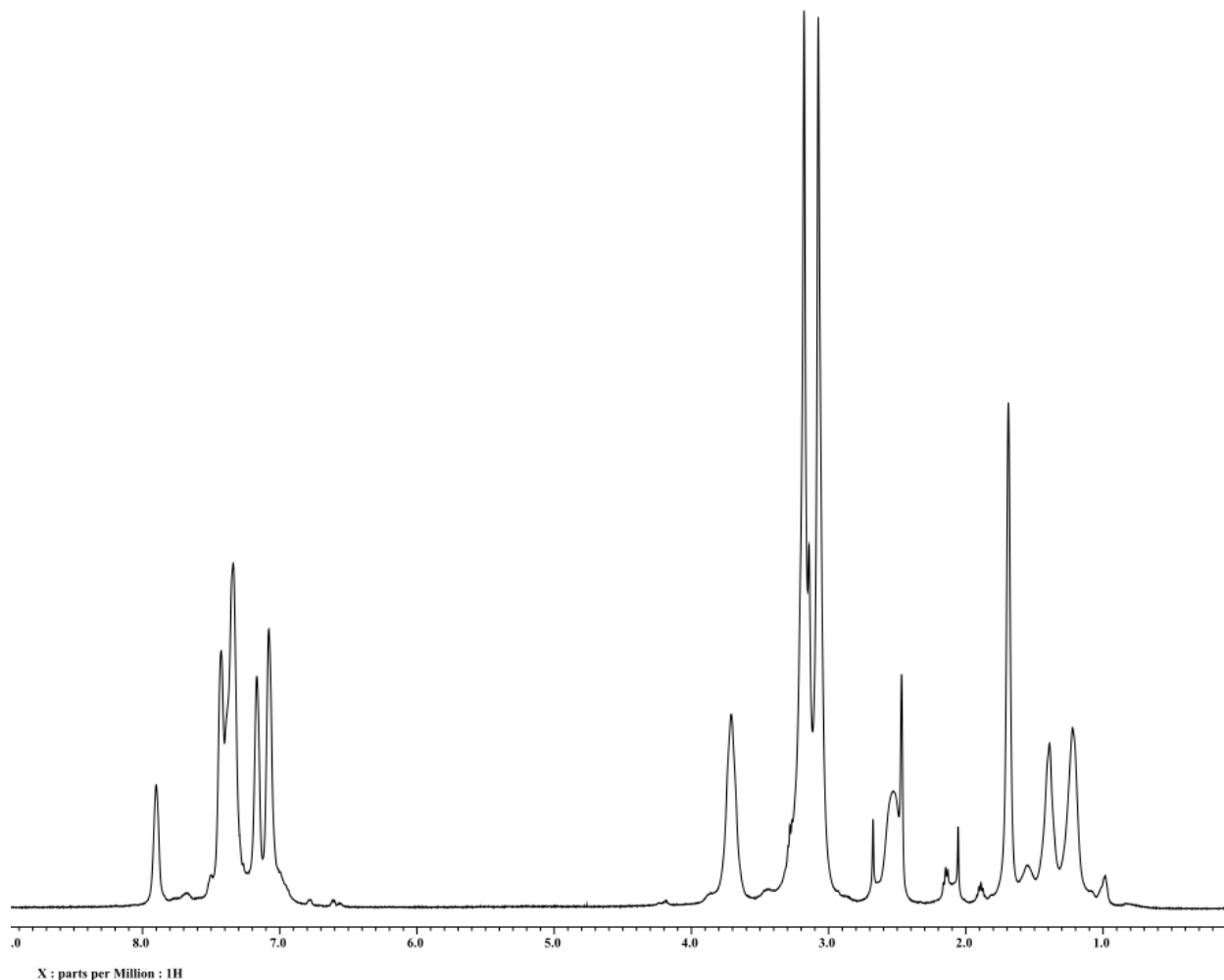


Figure 4.6 ^1H NMR spectrum of the 50 wt% PEI-PDADMA(PF₆).

Table 4.4 Compositions of the monomer feeds and copolymer products and yields for the PEI-PDADMA(PF₆) syntheses.

Trial	Monomer feed		Copolymer product		Yield [mass %]
	DADMA(PF ₆) [mole %]	DADMA(PF ₆) [mass %]	DADMA(PF ₆) [mole %]	DADMA(PF ₆) [mass %]	
1	43	21	33	16	85
2	53	31	52	30	92
3	64	41	65	42	94
4	72	51	72	51	85

Films cast from the polyetherimides had excellent physical properties, with those containing 20, 30, and 40 wt. % PDADMA(PF₆) demonstrating good strength, flexibility, and clarity. Additionally, because the copolymers can be isolated, characterized, and stored in the imide form, no significant degradation of properties was observed. As reported for the polyaramides, increasing the flexibility of the uncharged blocks significantly improved the material properties of the polymer films. Homopolyetherimide synthesized using the same procedure as the block copolymers was found to have a T_g of 217 °C, which is in excellent agreement with the literature value reported for Ultem®.⁴⁴ The T_g of the 40 wt. % PEI-PDADMA(PF₆) copolymer was slightly lower, at 201 °C, but still indicated that the multiblock copolymer has thermal properties very similar to those of the commercial polymer (Figures A.22-23).

The PEI-PDADMA(PF₆) multiblock copolymers demonstrated microphase separation morphology as determined by tapping mode AFM (Figure 4.7). There does seem to be some general increase in the amount and size of the light phases, which were determined to correspond to the PDADMA(PF₆) domains in the polyetheraramides analysis. Once again, the domains are disordered since no annealing step was performed. However, the correlation between the copolymer composition and microphases as identified by AFM is far less clear for the polyetherimides. This may be because the solubility of the polyetherimides in NMP is somewhat limited. As the film casting solution becomes very concentrated, small amounts of the copolymers may have begun to precipitate. This could disrupt the morphology of the films and would likely lead to a rougher film surface, which makes obtaining clear AFM images more challenging. Despite this, it is still clear that microphase separation was occurring within films of all compositions of the PEI-PDADM(PF₆) copolymers.

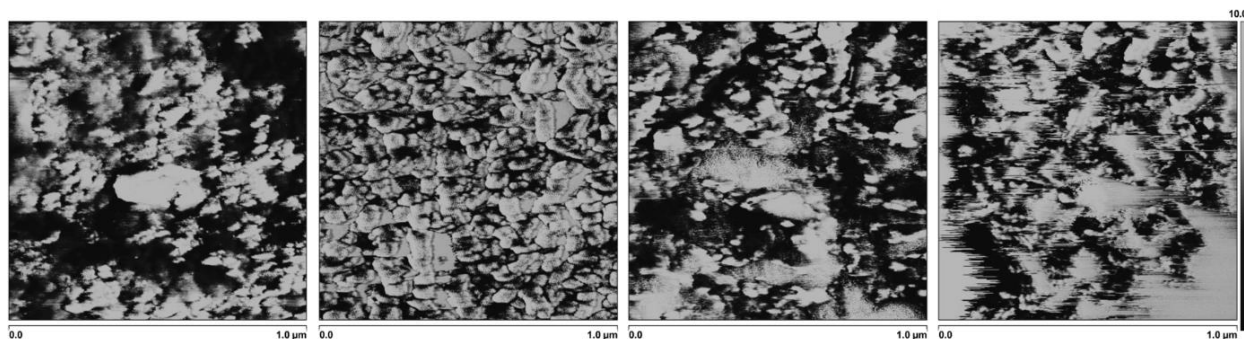


Figure 4.7 Tapping mode AFM phase images for the 20, 30, 40, and 50 wt. % PEI-PDADMA(PF₆) (left to right) copolymer films.

4.5 Conclusions

Multiblock copolymers were synthesized through the in-situ reaction of amine end-capped PDADMA(PF₆) oligomers with diamine monomers and either diacid monomers to produce polyaramides or dianhydride monomers to produce polyimides. The radical polymerization of DADMAC using bis(4-aminophenyl)disulfide as a photo-iniferter led to the formation of quantitatively functionalized oligomers of controllable molecular weight. Upon anion exchange from chloride to hexafluorophosphate, the oligomers became insoluble in water and soluble in polar aprotic solvents, making them suitable for the incorporation into hydrophobic, high-performance polymers. Multiblock polyaramides and polyimides were synthesized at a variety of compositions, and good agreement between the oligomer and monomer feed ratios and copolymer compositions indicated the successful difunctionalization and characterization of the PDADMA(PF₆) oligomers. The addition of ether linkages into the high-performance polymer segments increased the flexibility of the copolymer backbones and produced copolymers with improved film properties. Films of the PEA-PDADMA(PF₆) and PEI-PDADMA(PF₆) copolymers of 20, 30, and 40 wt. % PDADMA(PF₆) demonstrated good strength, clarity, and flexibility. This research represents a facile procedure for the synthesis of a variety of high-performance copolymer materials that contain both radically polymerized, charged blocks and step-growth polymerized, uncharged blocks. This method could be extended to produce a wide variety of novel multiblock copolymers.

4.6 References

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CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Summary and Conclusions

In the face of new and complex material challenges, the need for novel, advanced polymers is ever increasing. Polyelectrolytes are one important class of materials because they combine crucial properties of macromolecules with the unique electrostatic interactions and inherent conductivity of charged materials. For many applications, cationic polymer materials offer several unique advantages. Polymers based on quaternary heteroatom cations are often favored because they represent stable, permanent cationic groups.¹ Of the available quaternary cations, quaternary ammonium units are the most common due to their good stability and synthetic accessibility.² The unique benefit of DADMAC as an ammonium monomer is that it undergoes cyclopolymerization due to the diallyl structure.³ Because the cationic groups are incorporated into cyclic units within the polymer backbone, PDADMAC has improved alkaline stability over polymers containing pendant quaternary ammonium units.⁴ PDADMAC is an important polymer on an industrial scale for many applications, most notably as a flocculant in the treatment of contaminated water.⁵ DADMAC has been incorporated into a range of copolymers through a variety of mechanisms. However, the inherent difficulty of synthesizing copolymers containing components of different solubilities means that almost all DADMAC containing materials are water soluble. Since many polymer applications rely on the use of dimensionally stable, water insoluble polymeric films and membranes, the water solubility of DADMAC polymers and copolymers is significantly limiting.

The objective of this research was to determine successful mechanisms for incorporating diallyldimethylammonium units into novel, water insoluble copolymers. This process relied on the ability of DADMAC and PDADMAC to undergo counterion exchange.⁶ Conversion from chloride to the bulky, hydrophobic hexafluorophosphate ion produces a form of the monomer and polymer that is insoluble in water and soluble in polar aprotic solvents. The solubility of DADMA(PF₆) makes it possible to incorporate this form of the monomer or polymer into the synthetic systems required to produce hydrophobic polymers. In addition to insolubility in water, we targeted copolymers with membrane forming capacity. Polymeric membranes are extremely

important materials with applications in fields ranging from energy production to medicine. However, dry PDADMAC and PDADMA(PF₆) are very stiff and brittle, making the homopolymers unsuitable membrane materials. The incorporation of diallyldimethylammonium units into polymers known to produce robust films could result in a class of copolymers with a variety of interesting properties and possible applications. Two methods were examined to produce these copolymers: the radical copolymerization with a hydrophobic vinyl monomer and the incorporation of ammonium oligomers into multiblock copolymers synthesized via step-growth reactions.

Chapter 2 presents the synthesis of a copolymer of DADMA(PF₆) and MMA to address Hypothesis 1 (see p.29 Chapter 1). PMMA is a widely used polymer synthesized through radical polymerization, which forms optically clear, strong, and flexible films.⁷ In a previous report of the copolymerization of DADMAC and MMA in DMSO as a cosolvent, the reactivity ratio of MMA was determined to be orders of magnitude higher than that of DADMAC, making it difficult to prepare copolymers with a good incorporation of DADMAC units.⁸ In our work, the discovery was made that the water insoluble monomer salt DADMA(PF₆) is soluble in MMA, even at relatively high concentrations. As a result, bulk copolymerizations, which often favors higher conversion and better monomer incorporation, could be performed. The bulk copolymerization of DADMA(PF₆) and MMA was performed at a range of monomer feed ratios from 20 to 80 wt.% DADMA(PF₆). All ratios did successfully produce copolymer. At high conversion, quantitative ¹H NMR spectroscopy demonstrated good agreement between the monomer feed ratio and copolymer composition and the ability to produce copolymer with a stoichiometric majority of DADMA(PF₆) units. This represents one of the first reports of a copolymerization of a diallyldimethylammonium monomer and methacrylate monomer in which there was good incorporation of the ammonium monomer. Soxhlet extraction studies confirmed the tunability of copolymer composition as a function of monomer feed ratio but also indicated significant heterogeneity within the copolymer samples. A study of copolymer composition over reaction time showed that at short reaction times, and therefore low conversion, the average polymer chains were significantly enriched in MMA. As conversion increased, the average chain composition quickly approached the monomer feed ratio. The changing composition with regard to conversion indicated that, as previously reported, the reactivity ratio of MMA was higher than that of DADMA(PF₆), but the high conversion and monomer incorporation made possible by

bulk copolymerization allowed for good incorporation of both monomers in the final copolymer material. Copolymers of all compositions formed stand-alone films, with copolymers containing a higher ratio of MMA producing films with good flexibility and strength. The tunable composition of the copolymers therefore corresponds to tunable polymer properties. The results of this study support Hypothesis 1.

Chapters 3 and 4 focus on multiblock copolymers synthesized from functionalized PDADMA(PF₆) blocks. The objective of this work was to incorporate diallyldimethylammonium units into high-performance polymers to address Hypothesis 2 (see p.29 Chapter 1). The high-performance polymers (polysulfones, polyaramides, and polyimides) are materials known for producing membranes with exceptional strength, flexibility, and stability.⁹⁻¹¹ Polymers with both the excellent material properties of high-performance polymers and the base-stable cationic groups of DADMAC could be interesting for several applications. However, unlike the radically polymerized DADMA(PF₆), the high-performance polymers of interest are synthesized by step-growth mechanisms. To produce compatible copolymers of these two classes of materials, an iniferter-based multiblock copolymer synthesis was employed. Disulfide iniferters were synthesized then exposed to UV irradiation in a solution of DADMAC monomer, which caused the cleavage of the sulfur-sulfur bond to produce sulfide radicals that initiated the polymerization of DADMAC. Because sulfide radicals have a high chain-transfer rate and termination by recombination is favored in DADMAC polymerization, the results were telechelic DADMAC oligomers with end group functionality resulting from the iniferter chemistry. An additional benefit of iniferter-based synthesis is that good molecular weight control can be achieved by changing the iniferter to monomer ratio. The difunctionalized oligomers could function analogously to difunctional monomers in step-growth polymerizations thereby producing block copolymers containing both radical and step-growth polymer components. By properly selecting the iniferter functionality, it is possible to incorporate the polyammonium blocks into a variety of high-performance materials.

The first class of high-performance materials of interest, as discussed in Chapter 3, were polysulfones. Polysulfones are engineering polymers known for their excellent strength and chemical and thermal stability, which are synthesized by a nucleophilic aromatic substitution reaction between a dihalide and diphenol monomer.¹¹ To produce oligomers suitable for incorporation into polysulfones, bis(4-fluorophenyl)disulfide was used as the iniferter. After

oxidizing the sulfide end groups to sulfones and counterion exchanging the DADMAC units of the oligomer backbone to DADMA(PF₆), the oligomers were reacted in-situ with bisphenol A and bis(4-fluorophenyl)sulfone to produce multiblock copolymers. To understand the influence of composition on the copolymer properties, polymers containing 20, 30, 40, and 50 wt.% of the PDADMA(PF₆) oligomer were synthesized. All copolymer compositions formed films, and as was previously seen with the MMA copolymers, those with lower ratios of PDADMA(PF₆) had better material properties more like those of homopolysulfones. The ability to reproducibly synthesize the multiblock copolymers at high conversion, which was confirmed by high yields and good material properties, indicated that the oligomerization procedure did lead to quantitative difunctionalization. The results of the research presented in Chapter 3 represents not only the synthesis of novel cationic multiblock polysulfones, but a facile and reproducible technique for producing compatible copolymers containing segments produced through both radical and step-growth polymerization.

The iniferter-based synthesis can be expanded past polysulfones to prepare many classes of high-performance polymer materials if the iniferter functionality is selected properly. Since diamine monomers are useful for producing polymers with varied chemistries, we chose to focus on amine functionalized PDADMA(PF₆) oligomers for the work presented in Chapter 4. When bis(4-aminophenyl)disulfide was synthesized and used in the same manner as bis(4-fluorophenyl)disulfide, the oligomerization was unsuccessful. Since aromatic amines are known radical retarders, we chose to protect the amines with formamide groups before using the iniferter. The formamide iniferter was successfully used to produce PDADMAC oligomers of controlled molecular weight, which could then be deprotected to return the amine functionality. Once the oligomers were converted to the PF₆ form to yield the proper solubility, they were incorporated into polyaramides and polyimides. Both classes of polymers are commercially available high-performance materials used when very high thermal stability and strength are required.^{9,10}

To produce polyaramides, the amine-capped oligomers were reacted with *m*-phenylenediamine and isophthalic acid. While the synthesis did produce multiblock copolymer in good yield at a range of composition ratios, films of the copolymers were found to be very brittle. To reduce the entanglement molecular weight, the flexibility of the polyaramide portions of the copolymer was increased by replacing *m*-phenylenediamine with oxydianiline. The

resultant multiblock polyetheraramides, synthesized under the same reaction conditions and composition ratios, demonstrated much better film properties. Copolymers containing 20, 30, and 40 wt.% PDADMA(PF₆) formed films by drop casting with good clarity, strength, and flexibility.

Multiblock copolyimides were synthesized in-situ via a reaction between the amine capped PDADMA(PF₆) oligomers, oxydianiline, and pyromellitic dianhydride. When the aminolysis-based polymerization is performed, the initial result is a poly(amic acid), which can then be converted to the polyimide through a ring-closing reaction with the removal of water. For most polyimides, the poly(amic acid) form is soluble in organic solvents, but the polyimide is entirely insoluble. Therefore, the multiblock copolymers were isolated and characterized as the poly(amic acid)s, drop cast to produce films, and heated to facilitate imidization. In the imide form, the materials proved to have good strength but low flexibility. An additional concern was the susceptibility of poly(amic acid)s to degradation in the presence of residual monomer or solvent, which makes storage and use of the materials difficult.¹² To produce more flexible and soluble polyimides, pyromellitic dianhydride was replaced with bisphenol A dianhydride in the copolymer synthesis. The multiblock polyetherimides could be converted directly to the imide form in the polymerization solution and isolated, stored, and characterized as the polyimide. Additionally, as previously seen with the polyetheraramides, the increased flexibility of the polyimide blocks improved properties of the cast films. Films cast from NMP demonstrated good clarity, flexibility, and strength for the 20, 30, and 40 wt.% PDADMA(PF₆) polyetherimides. The results presented in both Chapter 3 and Chapter 4 support Hypothesis 2.

This body of research represents a variety of synthetic procedures for producing water insoluble copolymers containing the diallyldimethylammonium moiety. Additionally, to produce materials suitable for a variety of new applications, polymers capable of forming films and membranes were of particular interest. The studies were driven by the organic solubility of the hydrophobic DADMA(PF₆) monomer. Because DADMA(PF₆) is a diallyl monomer that undergoes radical polymerization, it was natural to begin copolymerization attempts with a vinyl comonomer. MMA was chosen because of the desirable properties of PMMA. We have demonstrated a facile, reproducible, bulk copolymerization of DADMA(PF₆) and MMA in which composition and material properties of the copolymers are highly tunable based on changing monomer feed ratios. The success of the initial radical copolymerization was

encouraging for the development of more complex copolymer systems. Specifically, we were interested in incorporating DADMA(PF₆) into high-performance polymer materials synthesized through step-growth polymerization to produce a class of materials with cationic character and excellent material properties. The combination of radical and step-growth polymerization was made possible through the initiation of DADMAC polymerization using difunctionalized disulfide iniferters, which produce difunctionalized oligomers. As with the radical polymerizations, the chloride counterions were converted to PF₆ to ensure solubility in the polar aprotic solvents necessary to synthesize high-performance polymers. PDADMA(PF₆) oligomers functionalized with fluorophenyl sulfone groups were incorporated into multiblock polysulfones and those functionalized with aminophenyl sulfide groups were used to produce multiblock polyaramides and polyimides. All three classes of block copolymers were synthesized at a variety of compositions and the properties of the resulting materials were closely tied to the relative amount of PDADMA(PF₆) in the copolymer. The multiblock copolymers formed films with good strength and flexibility at 20, 30, and 40 wt.% PDADMA(PF₆). Aside from producing materials with an interesting combination of properties, the iniferter-based multiblock copolymer synthesis is a very robust method for making copolymers containing segments produced through different polymerization mechanisms.

5.2 Recommendations for Future Work

A reasonable next step in the investigation of the DADMA(PF₆)-*co*-MMA copolymers is the ion exchange from PF₆ back to chloride or other hydrophilic counterions, the result of which would be amphiphilic copolymers with different solubilities at different compositions. An application of interest for these materials is as anti-biofilm coatings since DADMAC containing materials have known antibacterial properties.¹³ Additionally, the bulk copolymerization procedure could be extended past MMA to other vinyl monomers in which DADMA(PF₆) is soluble. 2-ethylhexyl methacrylate (EHMA) is one monomer of significant interest for future studies because PEHMA has a low glass transition temperature. Initial studies indicate that DADMA(PF₆) is soluble in EHMA, which would allow for bulk copolymerizations. A water insoluble, base stable, cationic polymer that is rubbery at room temperature could be an interesting material. Copolymerization of DADMAC with acrylamide followed by counterion exchange to PF₆ was shown to produce amphiphilic copolymers, which may demonstrate

swelling properties that are tunable with composition. Any number of other vinyl monomers could also be investigated as specific material properties become of interest.

The multiblock copolymers described herein are of interest because of the high positive charge density and base stability of the PDADMA(PF₆) blocks as well as the strength and stability of the high-performance polymer blocks. Additionally, the multiblock copolymers have demonstrated microphase separation, a process known to increase transport properties in polymer membranes.¹⁴⁻¹⁷ The possible applications of the multiblock copolymers are expanded greatly upon the counterion exchange from PF₆ to hydrophilic counterions such as chloride, hydroxide, carbonate, or bicarbonate. To facilitate the applications testing of the polymer membranes developed in this thesis, an effective strategy for the quantitative, post-synthetic counterion exchange is a necessary first step.

A significant field of interest for the application of robust, stable, cationic polymer membranes is in anion exchange membrane fuel cells (AEMFCs). AEMFCs, which generate power through hydroxide flux, have several benefits over their proton exchange counterparts, like the use of non-platinum catalysts and low activation energy, but they have not been shown to consistently demonstrate the same high-power density.^{18,19} To improve AEMFC performance, new anion exchange membranes with high alkaline stability, good physical strength, and hydroxide ion conductivity are being developed.²⁰⁻²⁴ Previous work in the Knauss group has demonstrated that multiblock polysulfones with poly(diallylpiperidinium hydroxide) blocks had ion exchange capacities that make them encouraging as membranes in AEMFCs.²⁵ The added base stability of the spirocyclic ammonium units in the piperidinium multiblock copolymers make them particularly suitable for AEMFC applications, and preliminary testing of these membranes in fuel cells shows encouraging performance and stability.²⁶ The multiblock polysulfones reported in Chapter 2 may have lower base stability, but they are still of interest due to the benefit of using a commercially available ammonium monomer. Beyond AEMFCs, the materials are expected to be useful as membranes in alkaline electrolysis applications.

The ion conductivity of the multiblock copolymer membranes also makes them materials of interest for solid state battery applications. Solid polymer electrolytes offer distinct advantages over conventional battery materials due to their increased safety and flexibility.²⁷ Quaternary ammonium copolymers have been investigated as materials for zinc,^{28,29} lithium,³⁰ and sodium³¹ batteries. Depending on the specific battery system of interest, different counterions have been

investigated. While the most promising is TFSI, one study did find the PF₆ form of the polymer to be effective as a binder in lithium-sulfide batteries.³⁰ The polysulfone, polyetheraramide, and polyetherimide copolymers presented in this work could all be suitable materials for solid state batteries because of their capacity to form strong, flexible films. Additionally, the somewhat lower water solubility demonstrated for PDADMA(TFSI)³² may indicate that it would be suitable for use in the developed multiblock copolymer syntheses. This should be investigated because, if it were so, it would eliminate the need for a secondary counterion exchange from the PF₆ form. Additionally, testing of the existing copolymer films in the PF₆ form for lithium-ion conductivity or preliminary battery performance is of significant interest.

As discussed in Chapter 2, the multiblock polysulfones have undergone initial testing as direct-air CO₂ capture materials. While the CO₂ capture capacities of the membranes in the moisture swing testing setup were significantly below the desired values, the growing need for CO₂ capture makes it an area of continues interest for these materials. Exploring different direct-air capture methods for the multiblock polysulfones or expanding the testing to the available multiblock polyaramides and polyimides could provide useful insight to the interaction between atmospheric CO₂ and polymer membranes of different chemistries. In addition to CO₂, the PDADMA(PF₆) units in the polymer backbones may provide affinity for other gasses, which could make them useful as gas separation membranes. The separation, purification, and capture of a variety of gasses is crucial in several industries including chemical feedstocks, natural gas, and packaging.^{33,34} The use of polymeric membranes for gas separation has become increasingly important in the past few decades, and of the possible polymer structures, polyimides have demonstrated the best performance.^{35,36} Block polyimides have been shown to have a particularly good combination of permittivity and selectivity.³⁷ The unique cationic nature of the multiblock polyimide membrane presented in Chapter 4 may provide for gas separation properties unlike those that have previously been reported. Therefore, future gas permittivity and selectivity testing of the polyimide membranes is encouraged.

Another benefit of cationic polymers is their antimicrobial properties. Polymers containing both cationic and hydrophobic components are known to disrupt bacterial cell membranes, causing the death of microbial organisms.³⁸ DADMAC containing polymers have been well studied for their antimicrobial effects.³⁹⁻⁴¹ Because high glass transition temperature polysulfones and polyimides are used in medical devices,⁴² producing inherently antibacterial

forms of these polymers could help reduce instances of infection in hospitals. The relatively high thermal stability of the DADMA blocks is anticipated to maintain overall thermal stability of the copolymers. However, initial testing of the cationic polysulfone membranes through series dilution⁴³ and a swab inoculation essay⁴⁴ demonstrated no statistically significant antibacterial activity against *E. coli*. The lack of activity may be a result of the PF₆ counterions, which could prevent the necessary interaction that is known to make DADMAC antimicrobial. Once again, the development of an effective anion exchange procedure may facilitate further applications of the copolymer materials.

The most important commercial application of PDADMAC is as a flocculant for water treatment.⁴⁵ Insoluble polymer membranes offer a different mechanism for the purification of contaminated water when flocculation is unsuitable. The dense multiblock copolymer membranes may prove suitable for pervaporation desalination.^{46,47} Layer-by-layer (LBL) deposition of PDADMAC and either poly(ether ether ketone)⁴⁸ or poly(styrene sulfonate)⁴⁹ onto ultrafiltration membranes has been shown to form nanofiltration membranes with excellent water treatment capacities. The use of block copolymers rather than homopolymers in LBL assemblies increases the number of possible electrostatic interactions in a given area, thereby lowering the number of layers necessary to achieve the same performance.⁵⁰ The LBL deposition of the reported block copolymers would produce materials with physical, ionic crosslinks interspersed between the hydrophobic polysulfone, polyaramide, or polyimide units. The novel materials resulting from the LBL synthesis may be useful for water purification or a variety of other applications.

While evaluating the existing polymer materials for suitable applications is of immediate interest, the fundamental focus of the research presented in this dissertation is less the specific materials described and more the versatile synthetic methods developed. As such, the copolymers presented in this work represent only a small selection of the possible structures that could be produced. In addition to the diamine and dihalide iniferters, 3,3'-dithiodipropionic acid was synthesized and shown to be an effective iniferter in the synthesis of PDADMA(PF₆) oligomers. Characterization of the carboxylic acid capped oligomers by ¹H NMR spectroscopy and titration found that they were of controlled molecular weight. Initial trials indicated that these oligomers may be suitable for incorporation into multiblock polyesters through the in-situ reaction with diacid and diisocyanate monomers. A variety of other iniferter functionalities, and

therefore copolymer chemistries, could be achieved due to the relative simplicity of synthesizing and employing disulfide iniferters. As new applications for water insoluble cationic membranes are tested and developed, the identity of the high-performance blocks can be tuned to make materials that are most suitable for each specific application.

Past the extension to novel ammonium containing block copolymers, the iniferter technique presents a method for producing an incredibly wide variety of materials. Though we focused on diallyldimethylammonium polymers due to their unique and beneficial properties, many vinyl monomers could be oligomerized and functionalized using iniferters. One interesting class of block copolymers are thermoplastic elastomers, which combine the properties of their hard and rubbery segments to produce strong materials with enhanced performances and lifetimes.⁵¹ Most thermoplastic elastomers are made through living radical block copolymerizations of vinyl monomers like styrene and isoprene or through the step-growth polymerization of hard and soft segment monomers like diisocyanates and polyols. The available types of thermoplastic elastomers could be expanded significantly by using the iniferter-based multiblock copolymer synthesis to combine the two classes of polymer synthesis. Properly chosen radically polymerized monomers can serve as either the hard or soft segments with a wide variety of step-growth polymer counterparts. Iniferters are additionally effective for producing oligomers of controllable molecular weight from monomers which are not suitable for controlled radical polymerization. Future work in this area should focus on utilizing the developed synthetic method to produce any number of novel block copolymers designed with specific properties and applications in mind. The work presented in this thesis should serve as the foundation upon which new and interesting classes of materials can be built.

5.3 References

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APPENDIX A

SUPPLEMENTAL FILES FOR WORK PRESENTED IN CHAPTER 4

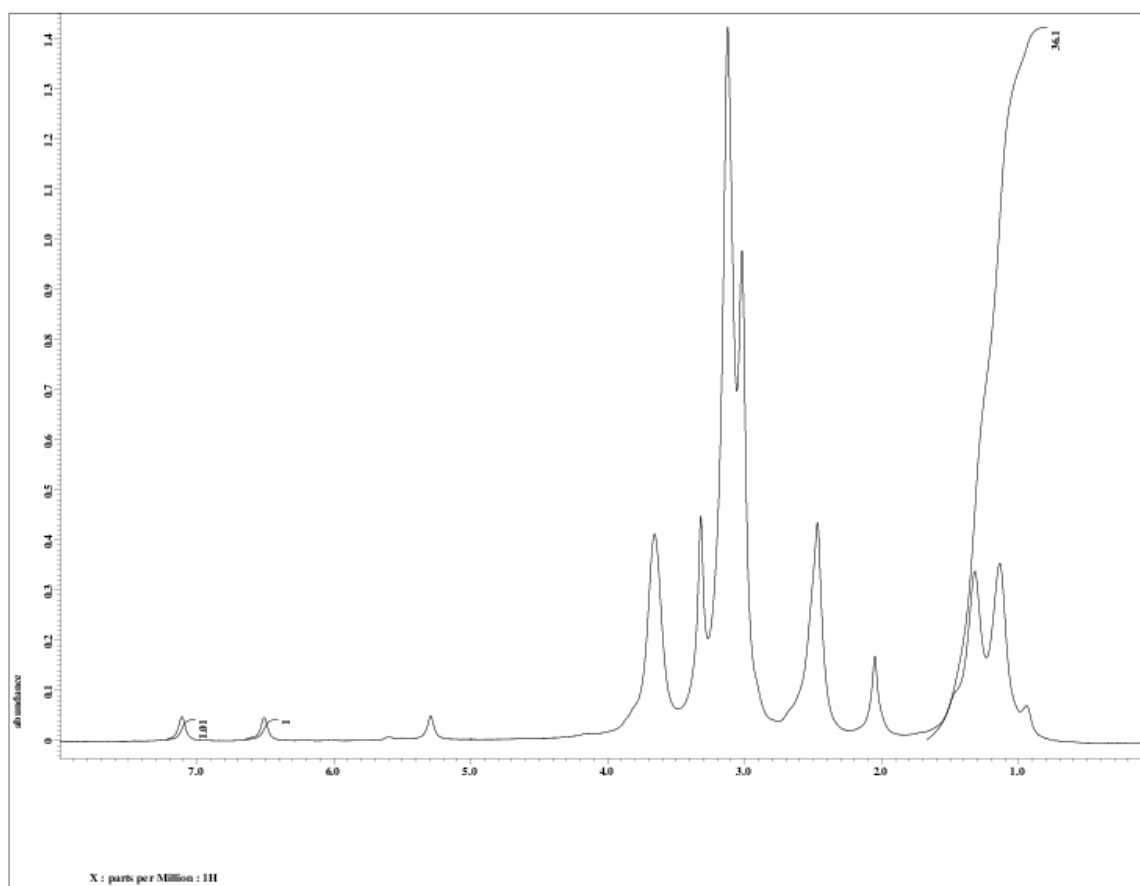


Figure A.1 ^1H NMR spectrum of the 36 repeat unit, amine functionalized PDADMA(PF_6) oligomer.

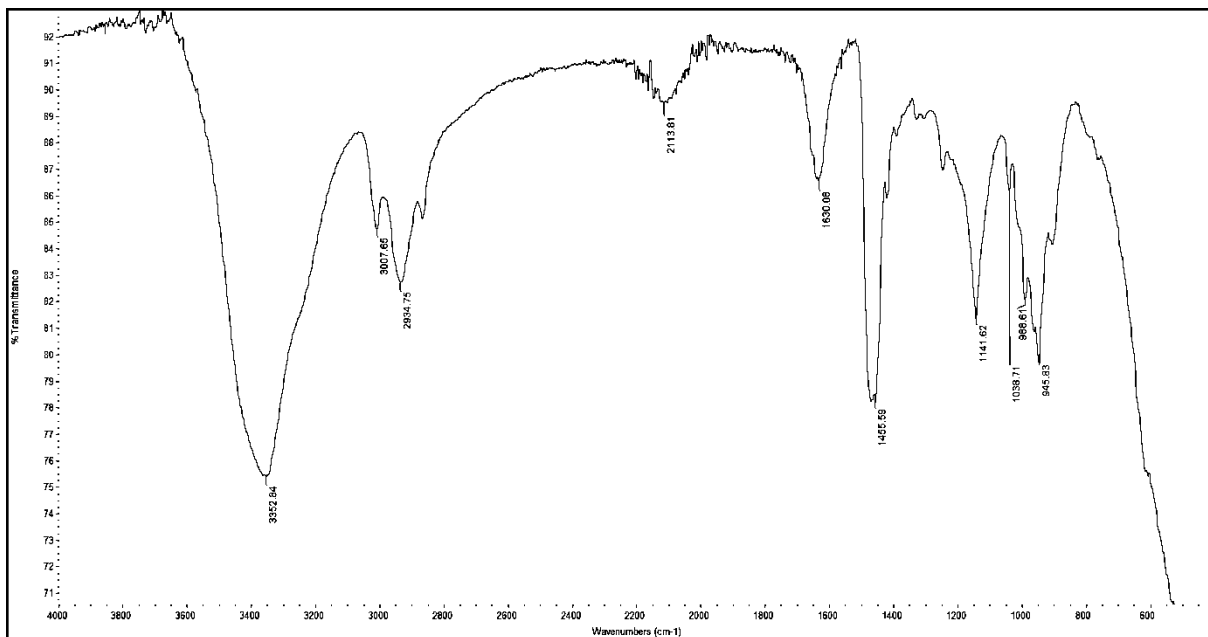


Figure A.2 FTIR spectrum of PDADMAC.

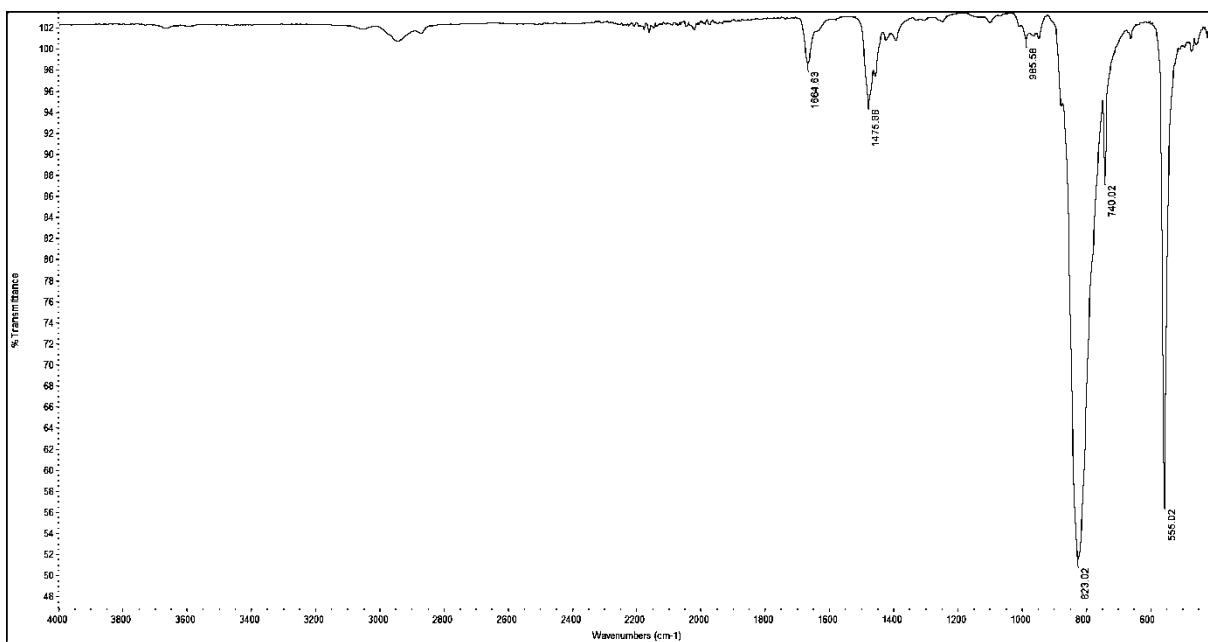


Figure A.3 FTIR spectrum of PDADMA(PF₆).

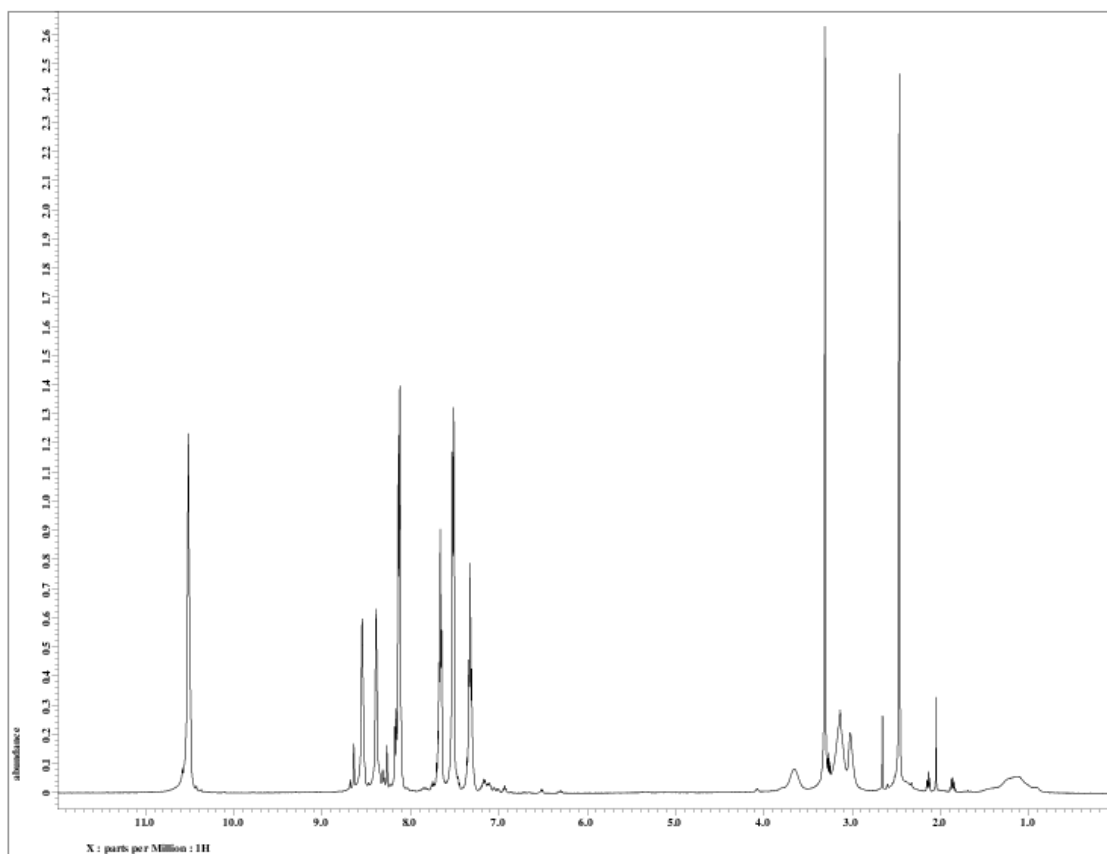


Figure A.4 ^1H NMR spectrum of 20 wt. % PA-PDADMA(PF_6).

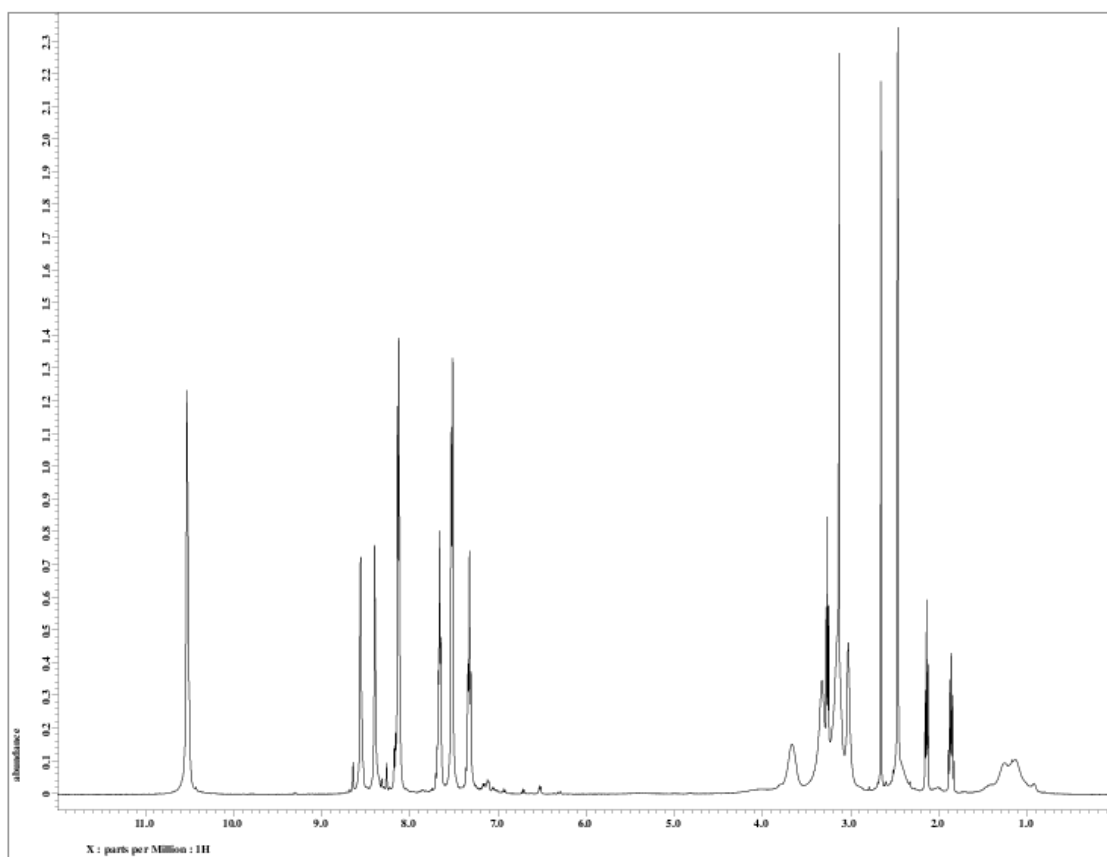


Figure A.5 ^1H NMR spectrum of 30 wt. % PA-PDADMA(PF_6).

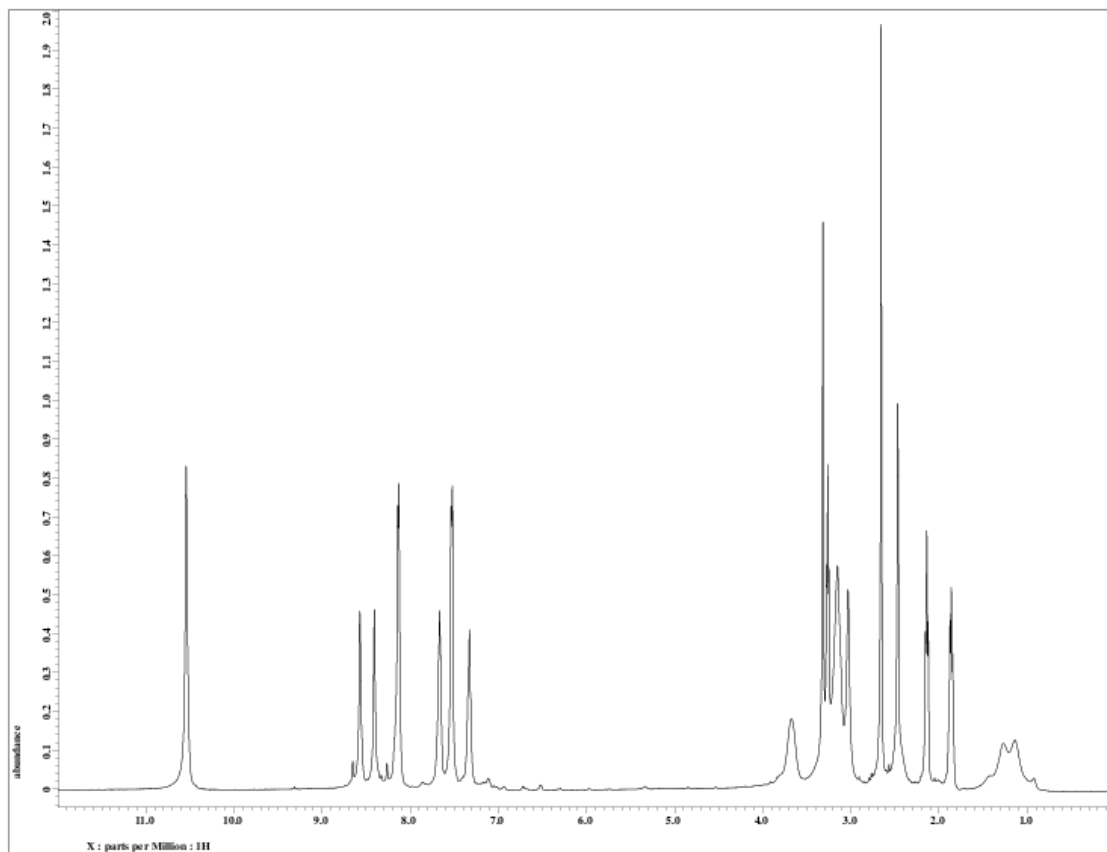


Figure A.6 ^1H NMR spectrum of 40 wt. % PA-PDADMA(PF_6).

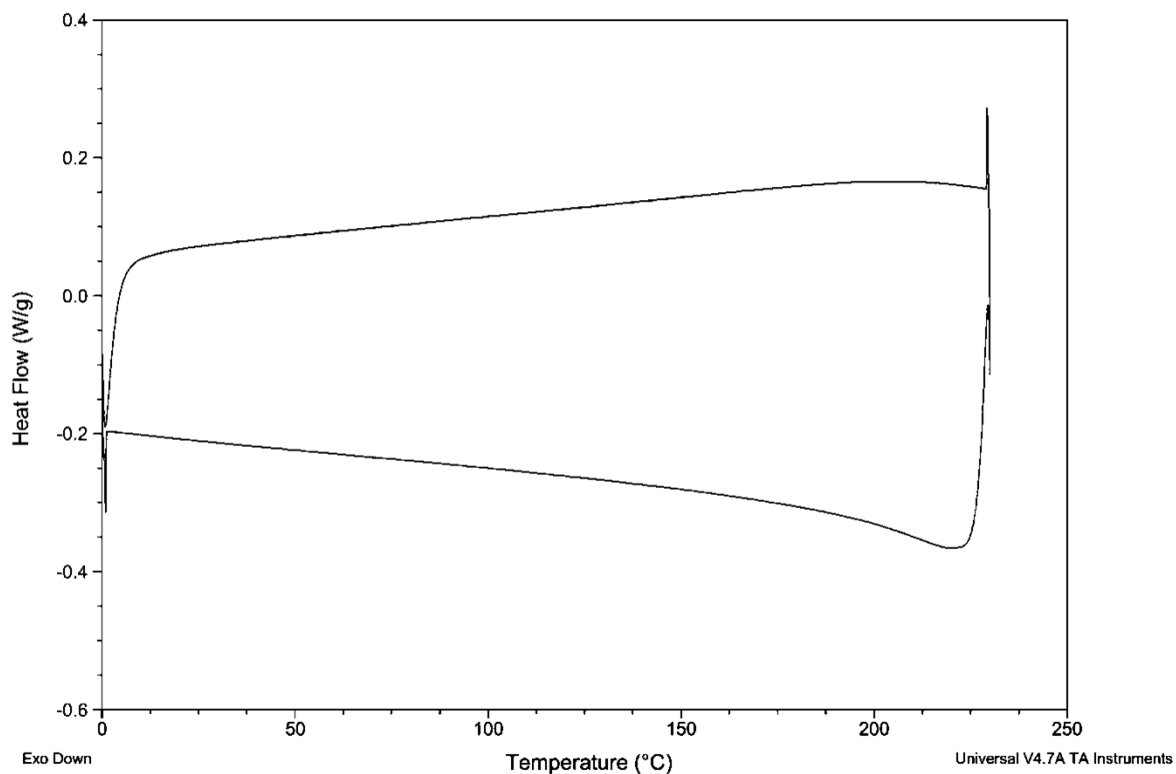


Figure A.7 DSC curve of 40 wt. % PA-PDADMA(PF_6), exo down.

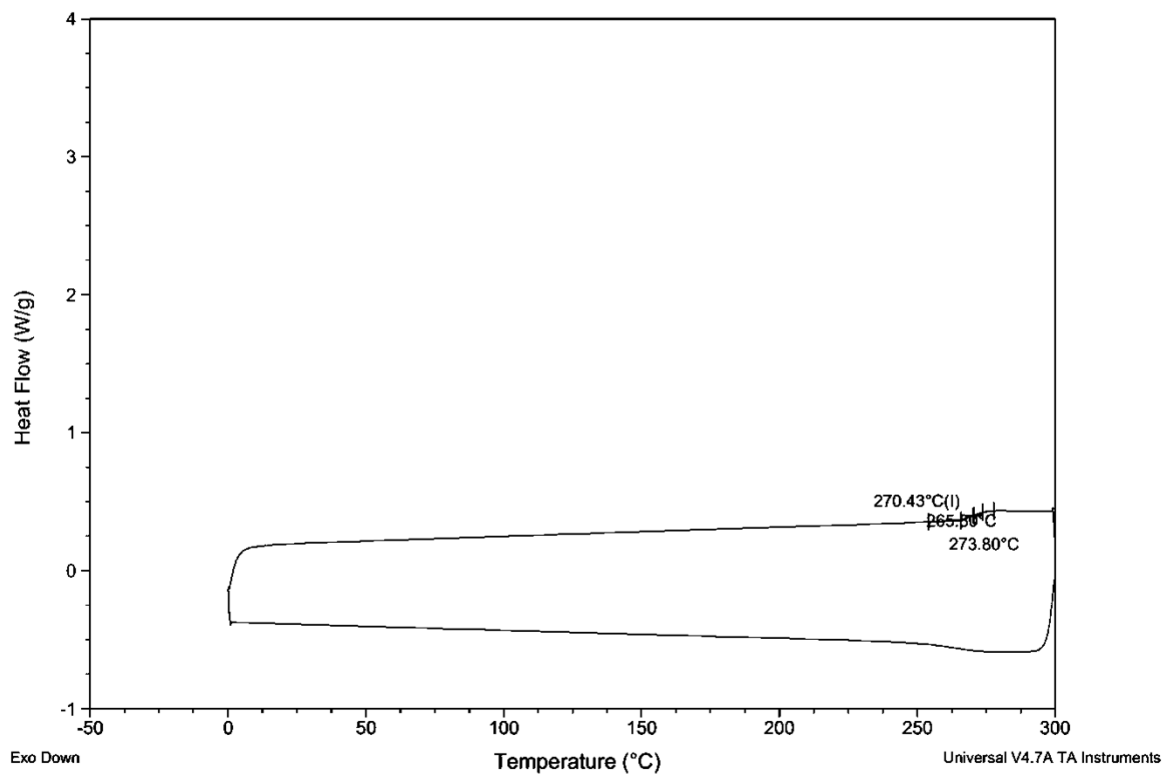


Figure A.8 DSC curve of homopolyamide, exo down.

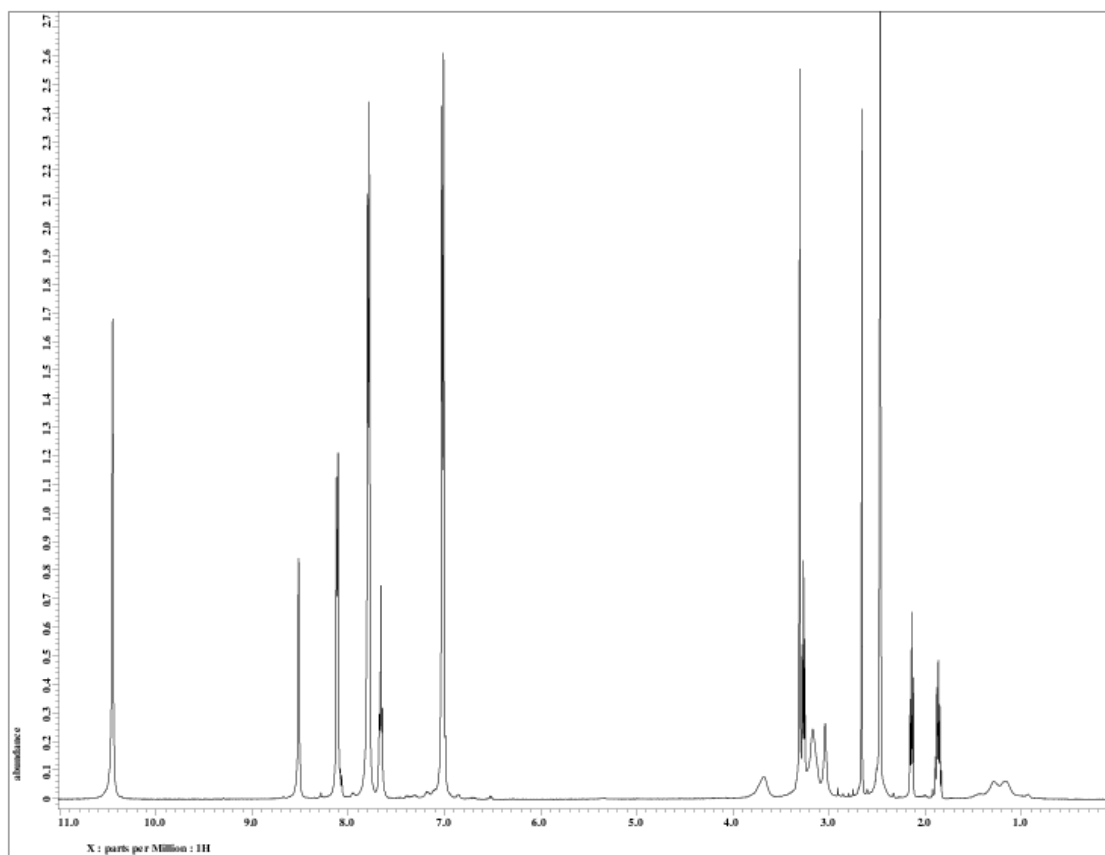


Figure A.9 ^1H NMR spectrum of 20 wt. % PEA-PDADMA(PF₆).

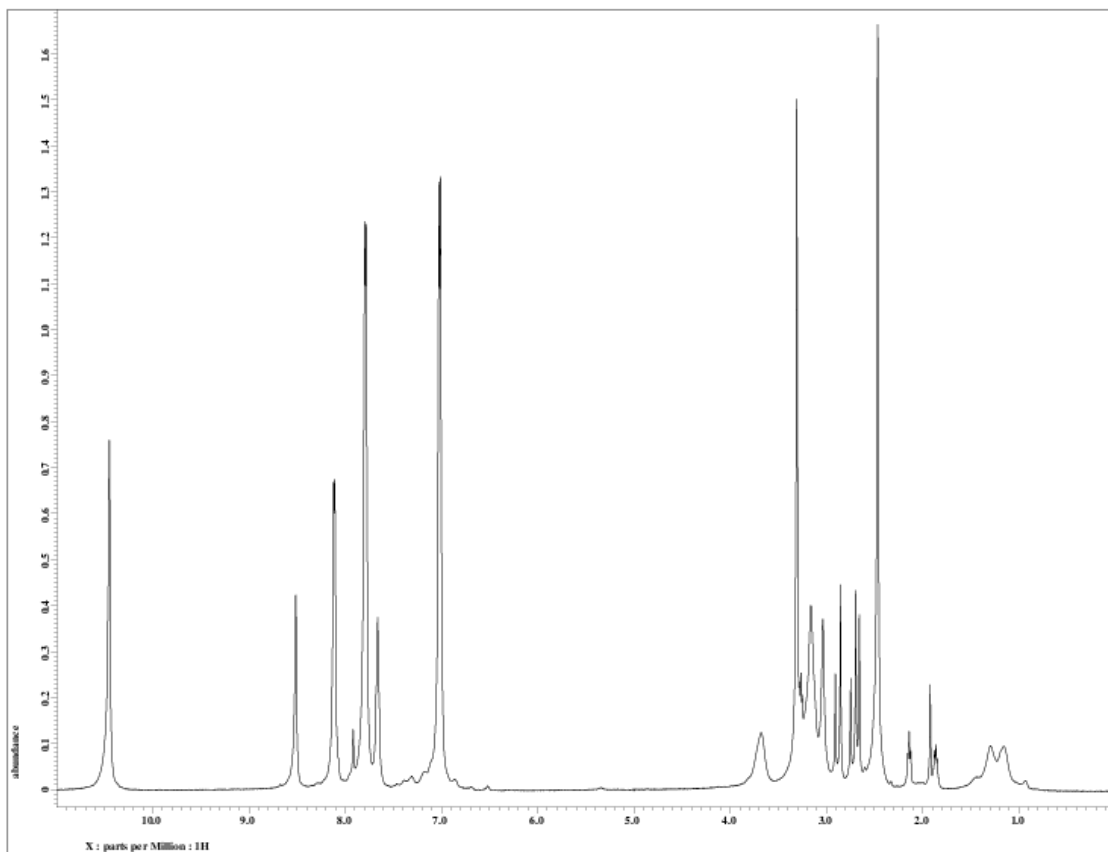


Figure A.10 ^1H NMR spectrum of 30 wt. % PEA-PDADMA(PF₆).

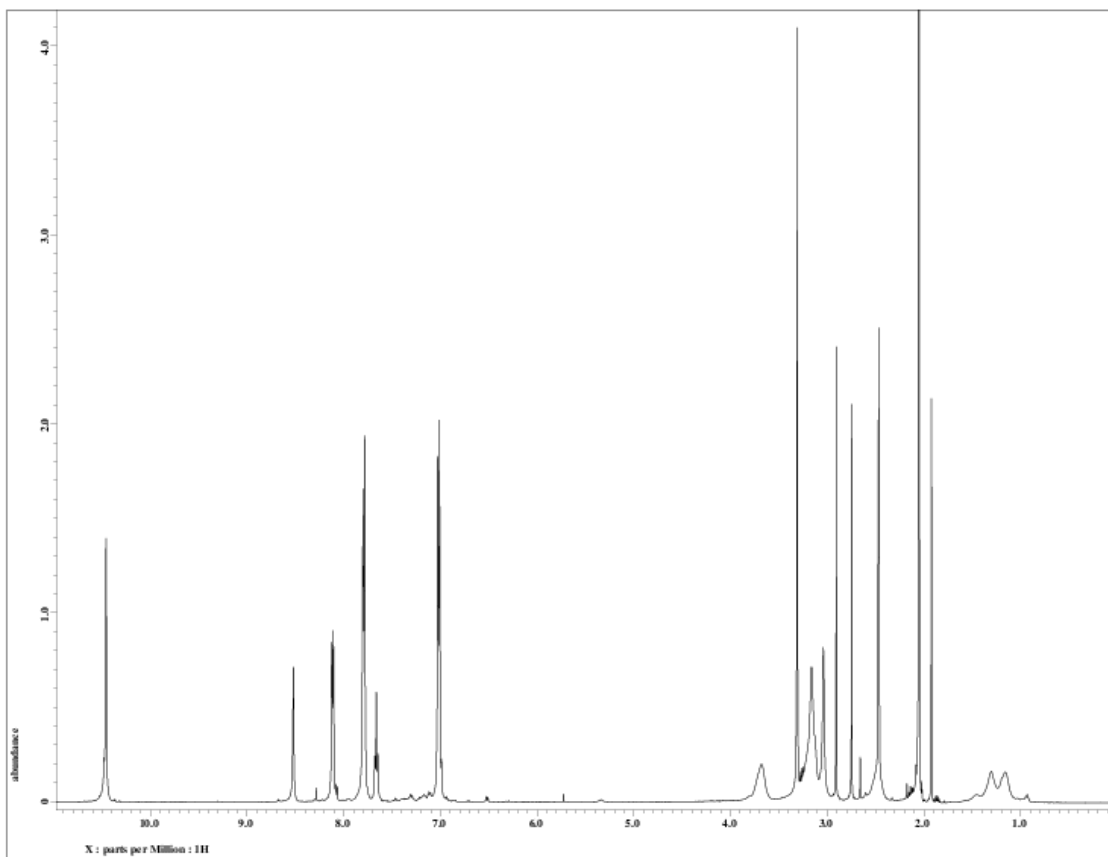


Figure A.11 ^1H NMR spectrum of 40 wt. % PEA-PDADMA(PF₆).

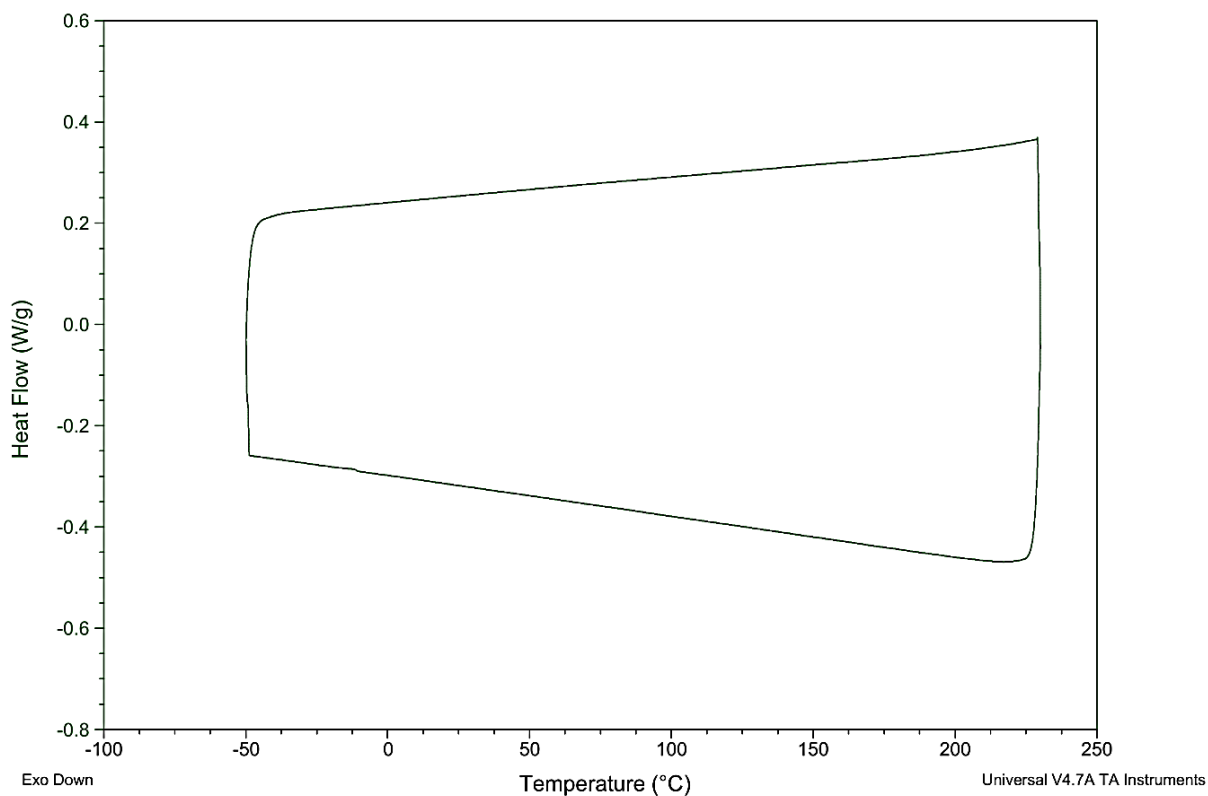


Figure A.12 DSC curve of 40 wt. % PEA-PDADMA(PF₆), exo down.

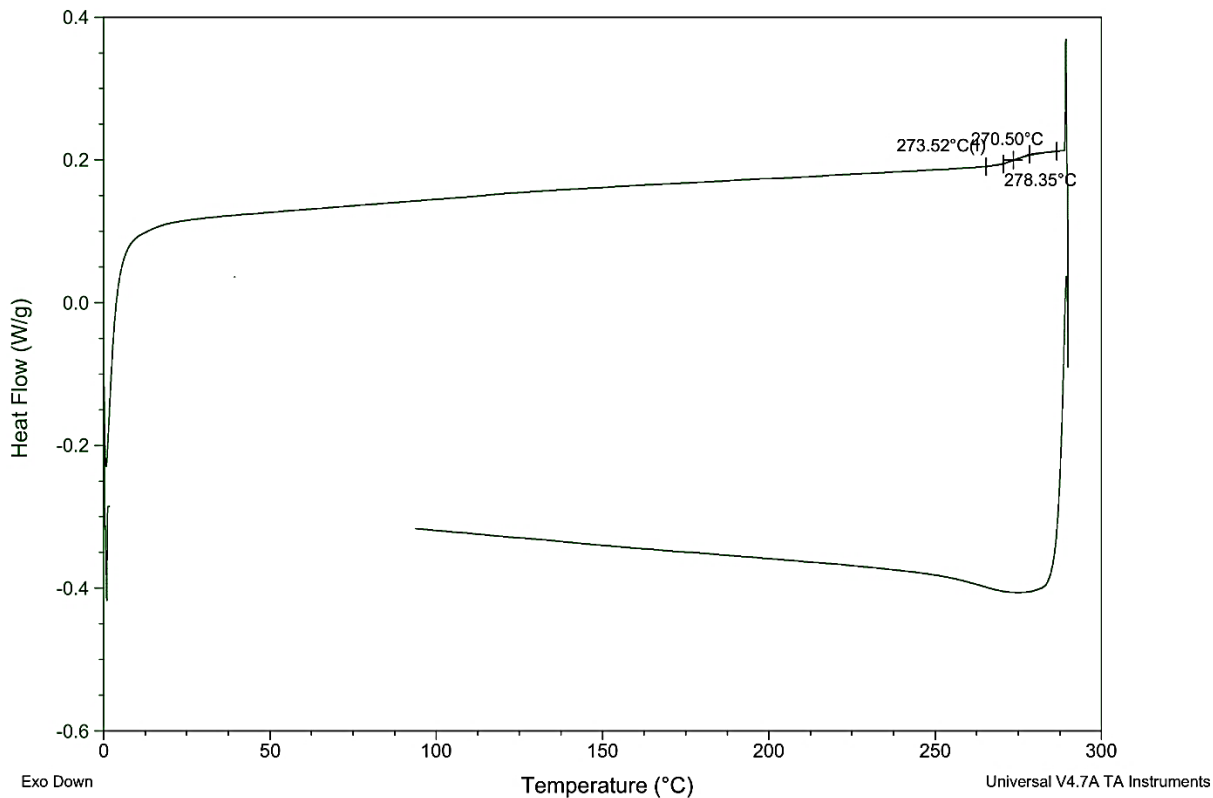


Figure A.13 DSC curve of homopolyetheraramide, exo down.

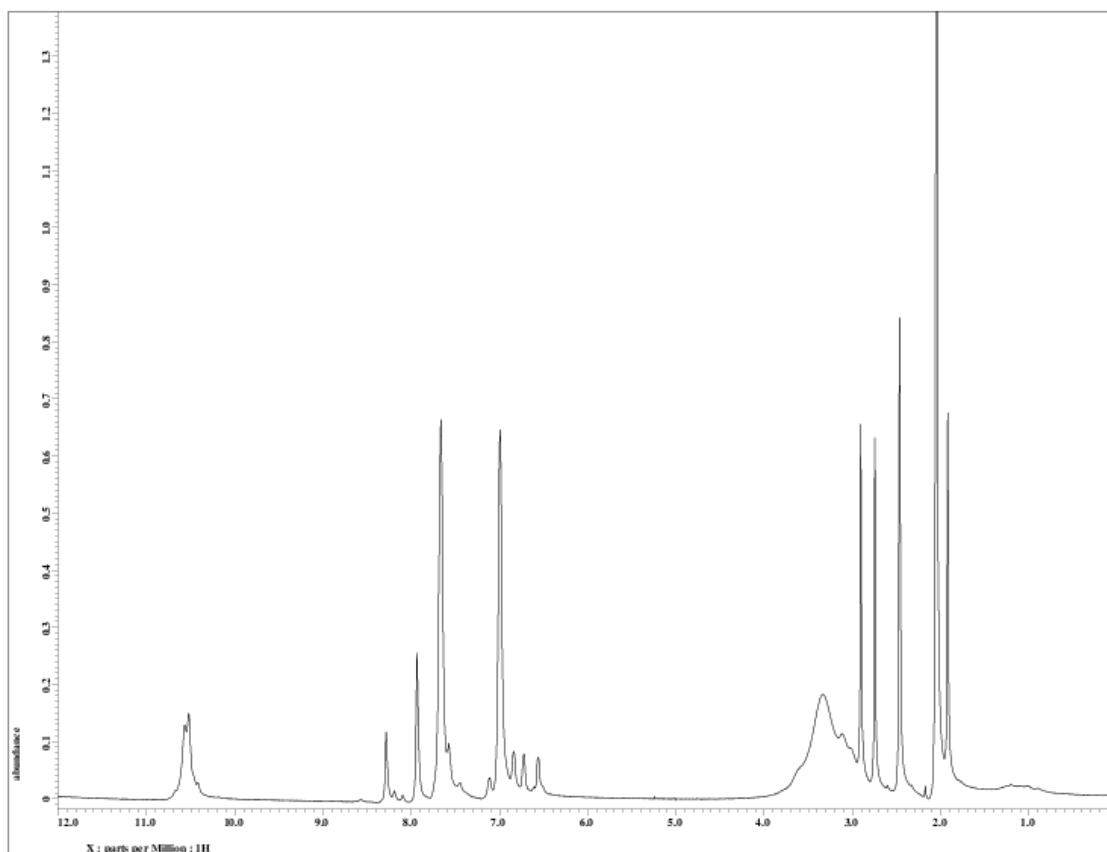


Figure A.14 ^1H NMR spectrum of 20 wt. % PI-PDADMA(PF₆).

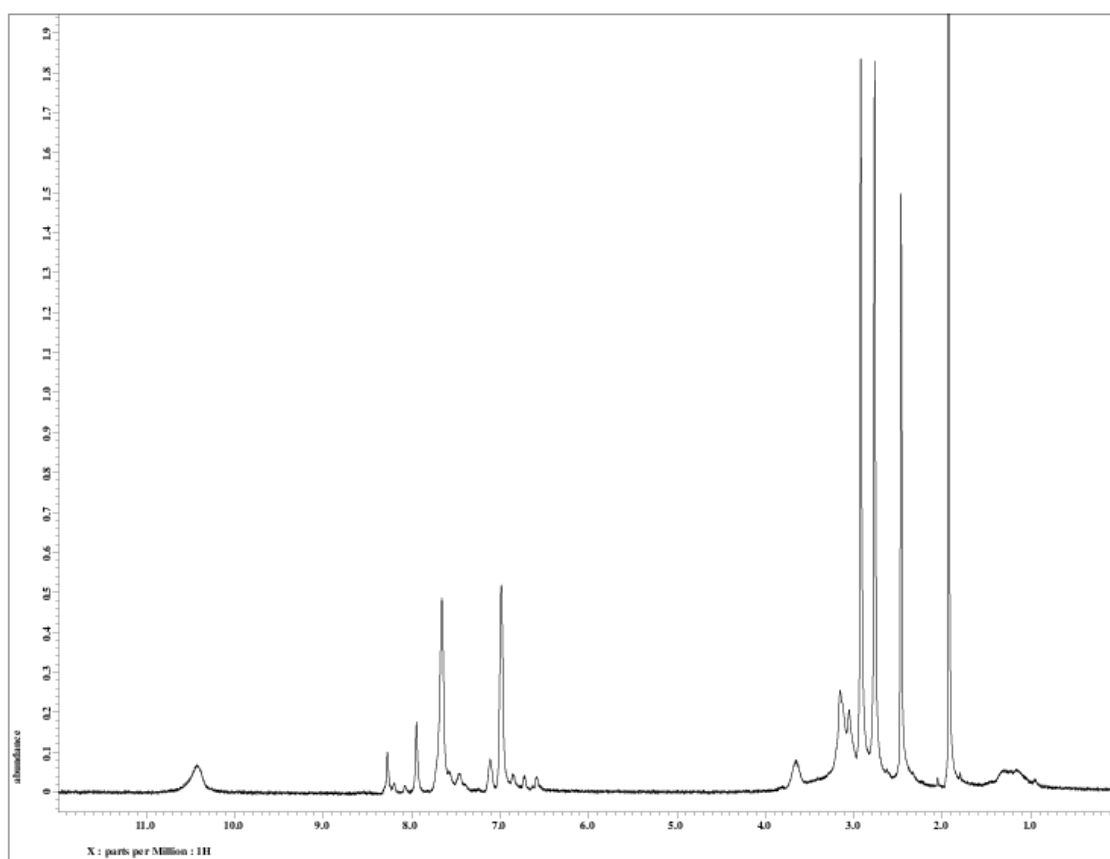


Figure A.15 ^1H NMR spectrum of 30 wt. % PI-PDADMA(PF₆).

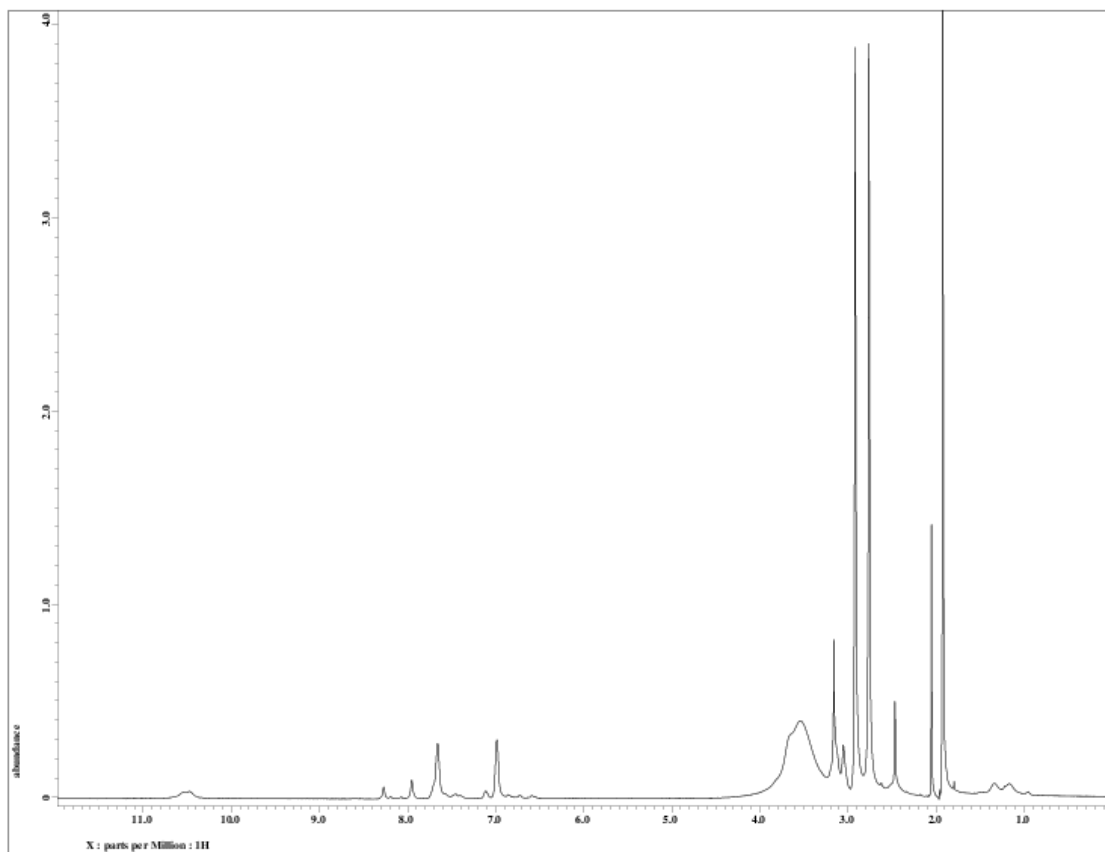


Figure A.16 ^1H NMR spectrum of 40 wt. % PI-PDADMA(PF_6).

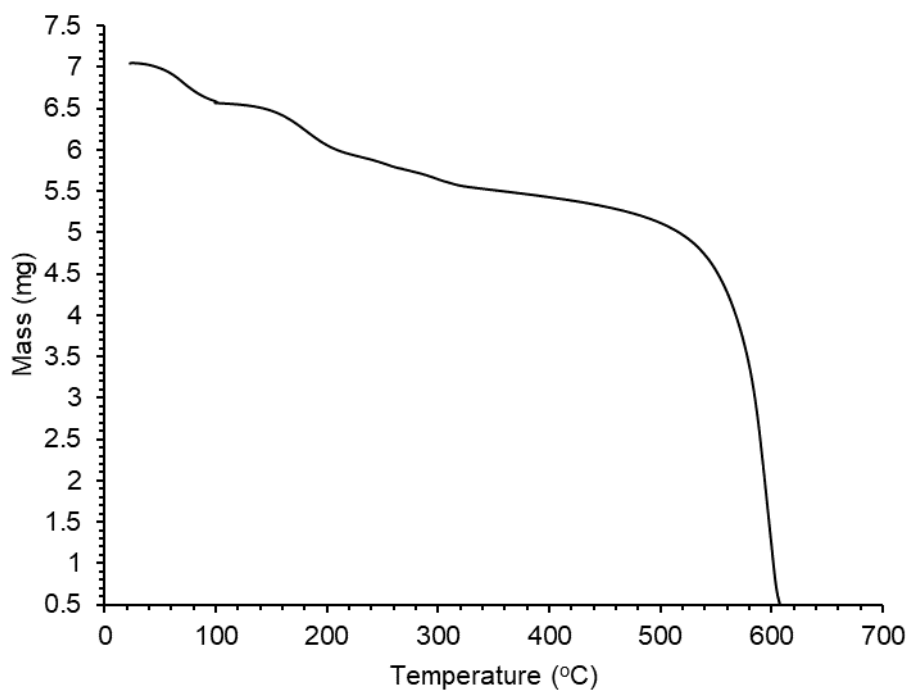


Figure A.17 TGA curve of 20 wt. % PDADMA(PF_6) multiblock poly(amic acid).

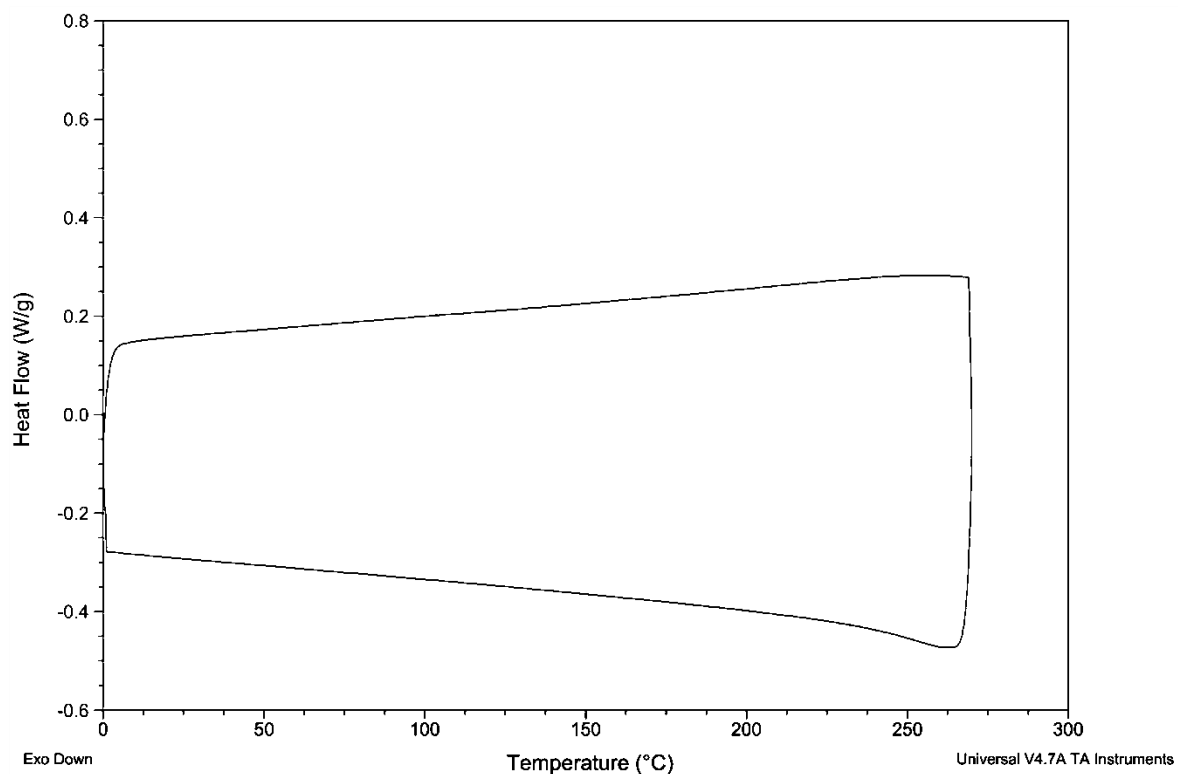


Figure A.18 DSC curve of 40 wt. % PI-PDADMA(PF₆), exo down.

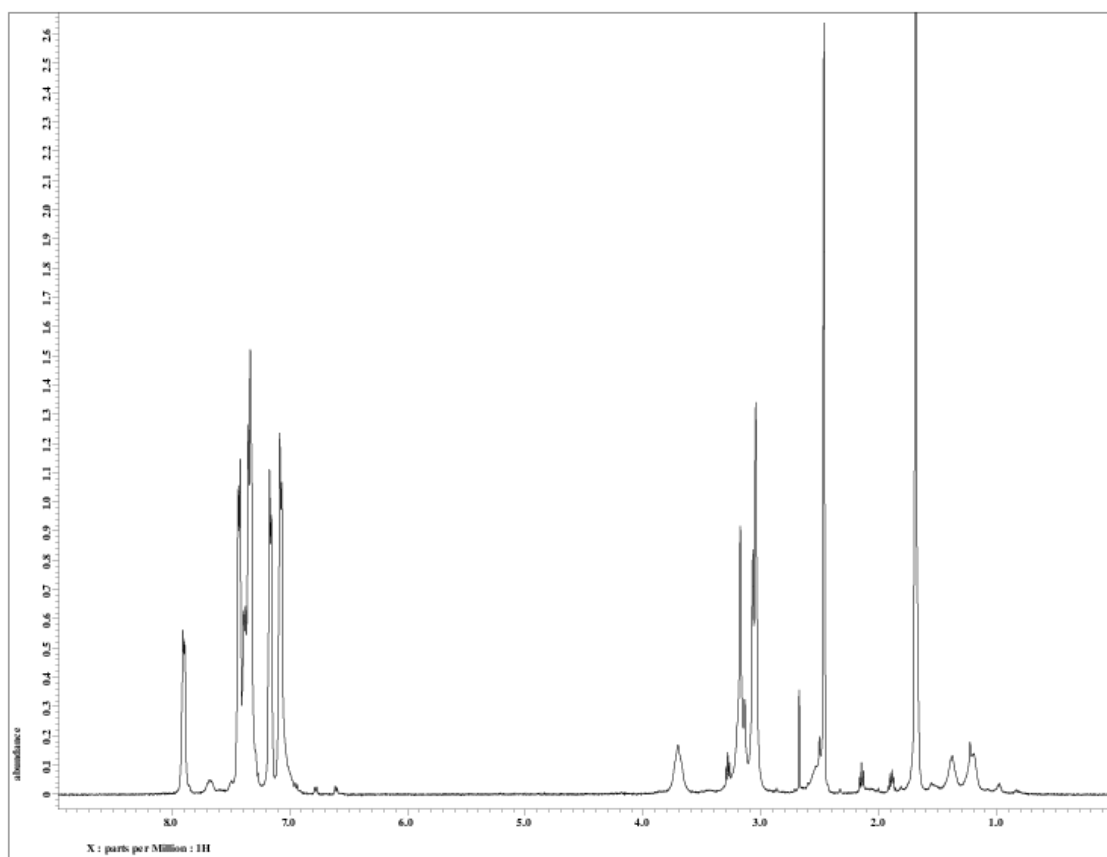


Figure A.19 ¹H NMR spectrum of 20 wt. % PEI-PDADMA(PF₆).

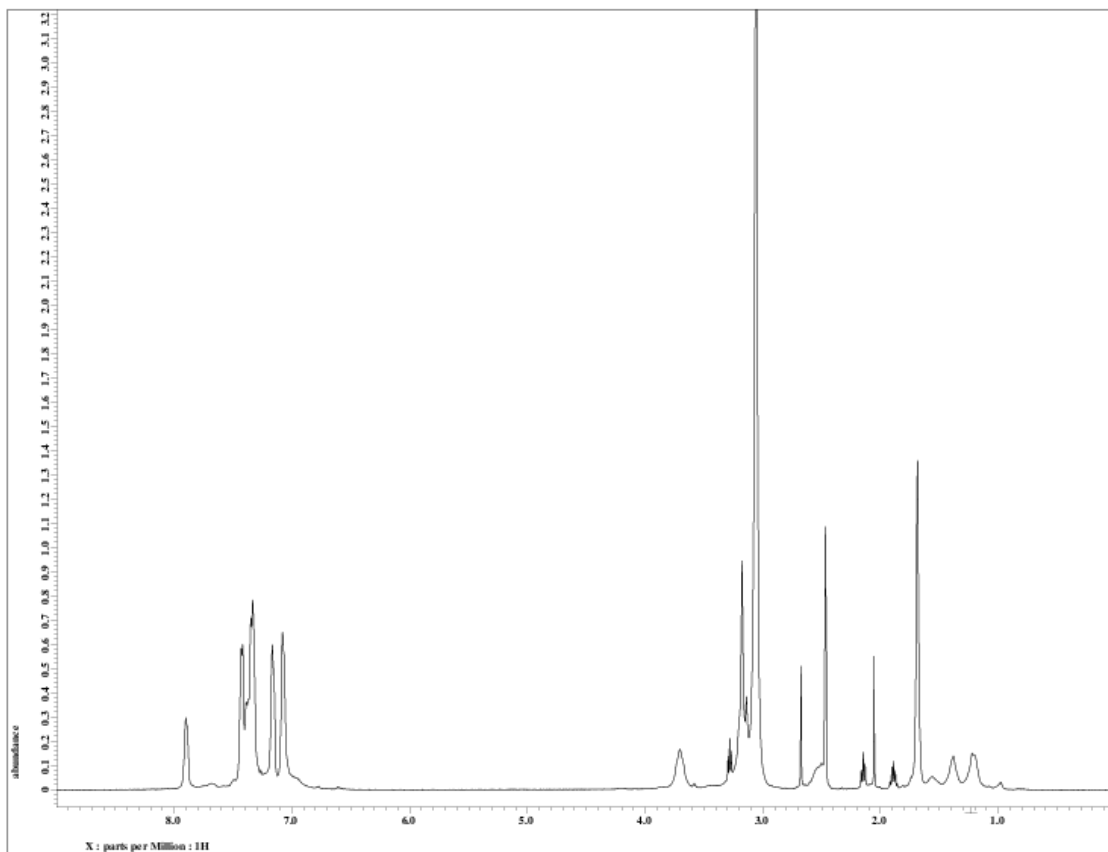


Figure A.20 ^1H NMR spectrum of 30 wt. % PEI-PDADMA(PF₆).

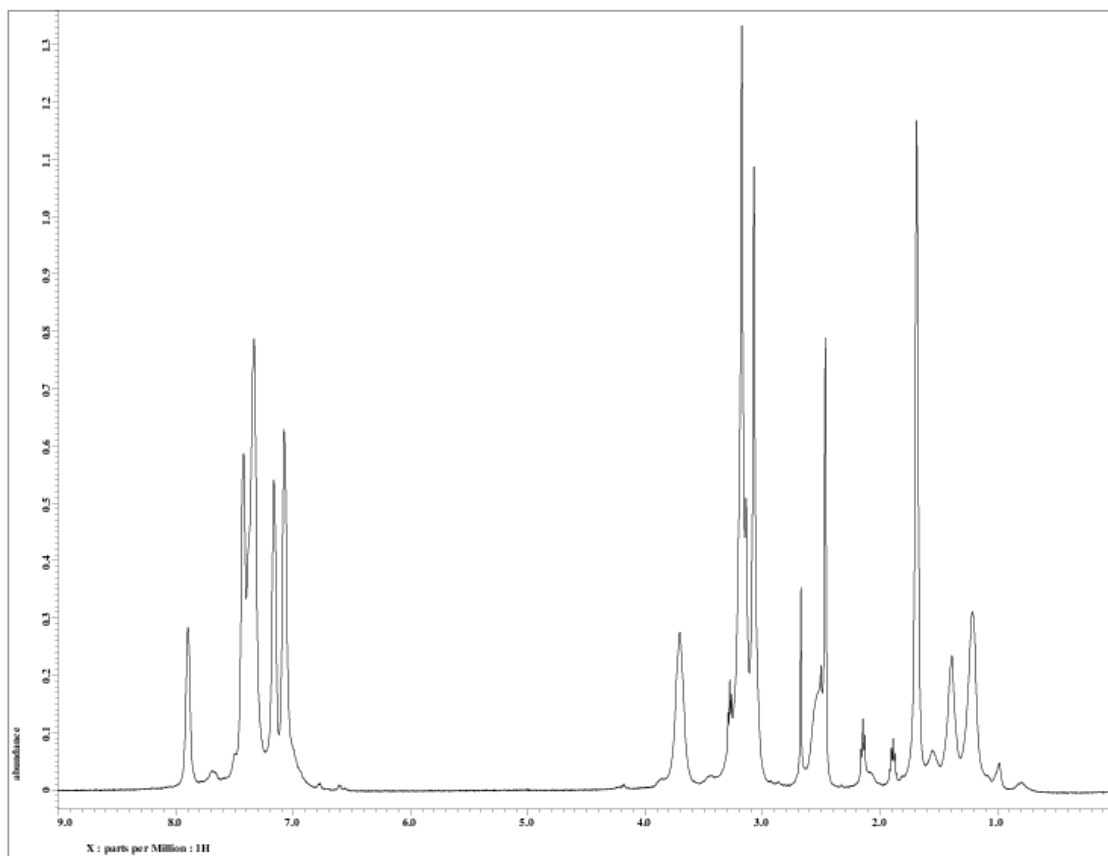


Figure A.21 ^1H NMR spectrum of 40 wt. % PEI-PDADMA(PF₆).

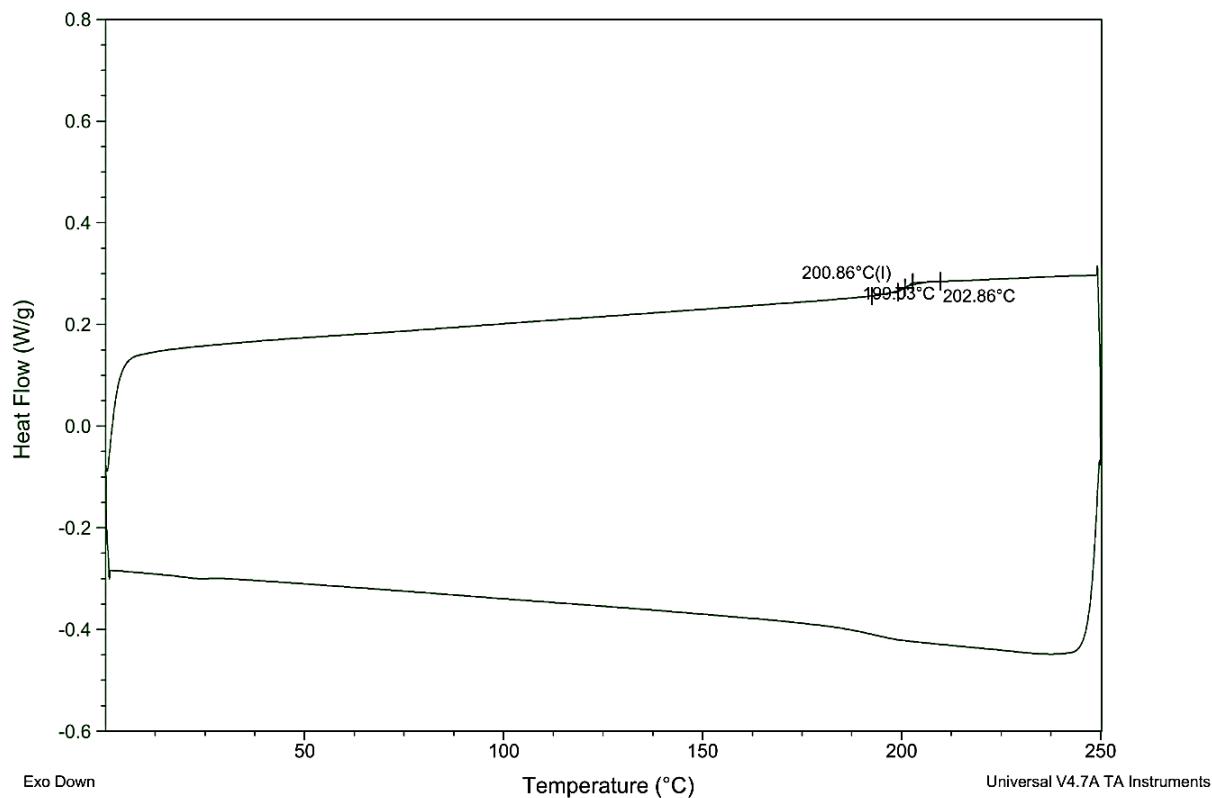


Figure A.22 DSC curve of 40 wt. % PEI-PDADMA(PF₆), exo down.

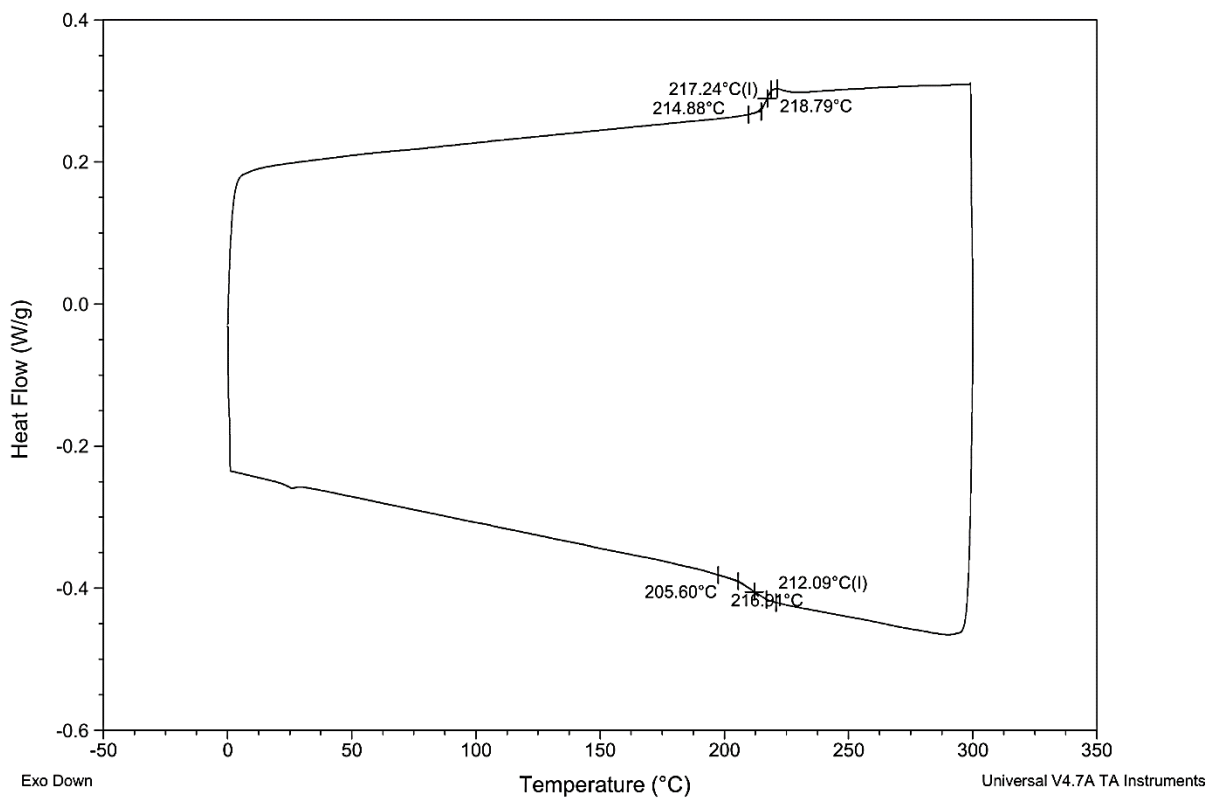


Figure A.23 DSC curve of homopolyetherimide, exo down.

APPENDIX B

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Author: Joel S. Olsson, Thanh Huong Pham, Patric Jannasch

Publication: *Macromolecules*

Publisher: American Chemical Society

Date: Apr 1, 2017

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