The Preparation of High Performance Polymers for Composites and Blends: A) Thermally Stable Ion Containing Polymers
B) Epoxy and Hydroxy Functional Polyolefin Macromers

by

John Victor Facinelli

Dissertation submitted to the Faculty of the Virginia Polytechnic Institute and State University in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY
in
Materials Engineering Science

Approved by:

Judy S. Riffle, Chair

J. E. McGrath
R. M. Davis

G. Wilkes
A. Shultz

May, 1996
Blacksburg, Virginia

Keywords: Polyimide, Poly(amic acid), Poly(arylene ether), Compatibilizer, Macromer
The Preparation of High Performance Polymers for Composites
and Blends:  A) Thermally Stable Ion Containing Polymers
B) Epoxy and Hydroxy Functional Polyolefin Macromers

John Victor Facinelli

Judy S. Riffle, Chair
Chemistry Department

(Abstract)

In this dissertation, two approaches were taken to design aqueous
dispersable or soluble high performance ion containing polymers to be used as
composite system interfacial modifiers and processing aids. In the first
approach, thermally stable pyridine containing poly(arylene ether)s were
designed which could be ionized by protonation in acidic aqueous media. A
novel pyridine containing bisphenol monomer, 2,6-(p-hydroxyphenoxy)pyridine,
was synthesized and utilized as a monomer for the synthesis of these pyridine
moiety containing, high performance polymers containing sulfone, sulfoxide,
phosphine oxide, ketimine, and ketone moieties. These pyridine containing
poly(arylene ether)s can function as electrostatic stabilizers, but not as the more
efficient steric stabilizers. The second approach endeavored to form controlled
molecular weight poly(ether-imides) via water soluble poly(amic acid) salt
precursors. In this approach controlled molecular weight poly(amic acid)s were
synthesized, and treated with stoichiometric quantities of tertiary or quaternary
ammonium bases to form poly(amic acid) salts. The imidization conditions, and
chemistry of the conversion of the poly(amic acid) salts to imide were studied,
with the aim of maintaining the targeted molecular weight distribution and properties analogous to a control polyimide.

For the above mentioned aqueous dispersion prepregging process, it is required that the matrix resin be in the form of small uniform particles capable of penetrating the interstices of a tight carbon fiber weave. Sub-μm dimension poly(ether ether ketone) (PEEK) particles useful for aqueous dispersion prepregging were prepared on a large scale by precipitation from high temperature solvent, quantitatively purified, and shown to display properties analogous to the commercial precursor material.

In the final chapter of this dissertation, the synthesis and characterization of a polyolefin macromer, and its incorporation into a polyester is detailed. These macromers, and the graft polymers resulting, have applicability in the area of polymer blend compatibilization.
Dedicated to

My Parents, Karen and Mario

My Sisters, Linda and Lorie

My Nieces and Nephews, Whitney, Clifton, Lydia, and Daniel
Acknowledgements

As with many research efforts within the National Science Foundation Center for High Performance Polymeric Adhesives and Composites, this work was conducted with the aid of many other students, and also full time Virginia Tech staff scientists. Thus, I want to extend my appreciation to all the students involved in the NSF Center and more, (especially Slade Gardner with whom I worked closely on this interdisciplinary project), for their invaluable help in my research. I would especially like to thank the excellent scientists who have assisted me in the characterization of many compounds and materials, specifically Tom Glass for his invaluable help with the Varian 400 mHz NMR, Steve McCartney for his excellent electron microscopy, Kim Herrich for Mass Spectral Analysis, and also Dr. Limin Dong for analysis of samples by Size Exclusion Chromatography. I would also like to thank those within Professor Riffle’s research group, especially Dr. J. R. Babu, Dr. Andrew Brink, Chenghong Li, Dr. Stephen Davis, Hui Li, and Dr. Venkat Venkatesan, for their everyday discussions and guidance. There were also two summer interns who contributed key parts to this research effort, Ping Chi, and Christy Sensenich, and I would like to thank them, and wish them success in their careers. Thanks also to Scott Harding for carrying out the large scale precipitation of poly(ether ether ketone) at Maxdem Corporation.

In addition to those who have helped me in this research I would like to acknowledge the excellent faculty at Virginia Tech from whom I have learned much, and particularly my advisory committee, Professor James E. McGrath, Dr. Allan Shultz, Professor Richey Davis, and Professor Garth Wilkes.
There are several key people to whom I am greatly indebted to for their motivation, inspiration and guidance. First I would like to acknowledge Dr. Phillip Kumler from SUNY, Fredonia who first introduced me to the fascinating subject of polymer chemistry in an undergraduate lecture course. Also I would like to heartily thank Dr. Scott George, my mentor during two summers spent in the Polycondensation Research Laboratories at Eastman Chemical Company for the fine example that he set for me of a research scientist in industry. I would also like to thank Professor Jerry Aducci, my advisor during a Masters of Science program at the Rochester Institute of Technology. Most of all I would like to thank my advisor Professor Judy Riffle for her great support, advice, and example throughout my years as a graduate student at Virginia Tech.
Table of Contents

Chapter 1 - Scope of Dissertation ................................................................. 1

Chapter 2 Pyridine Containing Poly(arylene ether)s ........................................ 2

2.1. SYNOPSIS ............................................................................................... 2

2.2. INTRODUCTION ...................................................................................... 3

2.2.1 Thermoplastic Carbon Fiber Composites From Fine Particles ................................ 3

2.2.2 Nature of the Approach ..................................................................... 6

2.2.3 Stabilization of Colloidal Dispersions ............................................... 6

2.2.4 Structure-Property Relationships in Poly(arylene Ether)s ...................... 12

2.2.5 Polymerization Mechanisms Of Poly(arylene Ether)s ....................... 12

2.2.6 Pyridine Containing Polymers as Polyelectrolytes .............................. 25

2.3. EXPERIMENTAL ................................................................................ 32

2.3.1 Materials.......................................................................................... 32

2.3.2 Model Study ..................................................................................... 34

2.3.3 Monomer Synthesis (2-Chloro-6-(4-hydroxyphenyl ether) pyridine) ......... 34

2.3.4 Monomer Synthesis (2,6-Bis(4-hydroxyphenyl ether) pyridine) .......... 36

2.3.5 2,6-Bis(4-hydroxyphenyl ether) Pyridine Purification ....................... 37

2.3.6 Synthesis of Pyridine Containing Poly(arylene ether)s .................... 39

2.3.7 Second Precipitation of the Pyridine Containing Poly(arylene ether)s .... 42

2.3.8 Dispersion of Pyridine Containing Poly(arylene ether)s in Water .......... 43

2.3.9 Characterization of Pyridine containing Copolymers ....................... 43

2.4. RESULTS AND DISCUSSION ................................................................. 44

2.4.1 Model Study of Reactivity of 2,6-Dichloropyridine ............................. 44
Chapter 3. Preparation of Controlled Molecular Weight Polyimides from Poly(amic acid) Salt Precursors

3.1. SYNOPSIS.................................................................................................93
3.2. INTRODUCTION........................................................................................95
  3.2.1 Condensation Polyimides.................................................................95
  3.2.2 Molecular Weight Control in Synthesis of Poly(amic acid).............................................................................99
  3.2.3 Imidization of Poly(amic acid)..........................................................107
  3.2.4 Polyamic Acid Derivatives.................................................................113
  3.2.5 Molecular Weight Characterization of Poly(amic acid) and Polyimides by Size Exclusion Chromatography.......122
3.3. EXPERIMENTAL ......................................................................................126
  3.3.1 Materials and Their Purification.......................................................126
  3.3.2 Synthesis of Poly(amic acid) in NMP by a Homogeneous Method.................................................................................129
  3.3.3 Synthesis of Poly(amic acid) in THF by a Homogeneous Method.................................................................................130
  3.3.4 Determination of Wt. % Solvent in Poly(amic acid).......................131
  3.3.5 Preparation of Poly(amic acid) Salts...............................................132
  3.3.6 Thermal Imidization of Poly(amic acid) Salts.................................134
3.3.7 Determination of the By-products from Melt imidization of Poly(amic acid) Salts .................................................134
3.3.8 Analysis of Imidization By-products by Gas Chromatography-Mass Spectrometry ..................................................136
3.4. CHARACTERIZATION.................................................................................................................................136
  3.4.1 Size Exclusion Chromatography .........................................................136
  3.4.2 Thermal Gravimetry ........................................................................137
  3.4.3 Differential Scanning Calorimetry ..................................................137
  3.4.4 Potentiometric Titration of Polyimides for Residual Amine .................................................................138
3.5. RESULTS AND DISCUSSION .........................................................................................................................139
  3.5.1 Theoretical $<M_n>$ vs. Time for Poly(amic acid) Synthesized in NMP and THF ..............................................143
3.6. CONCLUSIONS .............................................................................................................................................170
3.7. RECOMMENDATIONS FOR FUTURE WORK .............................................................................................171
3.8. REFERENCES ..................................................................................................................................................171

Chapter 4  Fine (Sub-$\mu$m) Poly(ether ether ketone) Powders ..........177
  4.1. INTRODUCTION .................................................................................................................................177
  4.2. EXPERIMENTAL .................................................................................................................................179
    4.2.1 Materials and Apparatus ..............................................................................................................179
    4.2.2 Particulate Formation .................................................................................................................181
    4.2.3 Purification of the PEEK powder .................................................................................................182
    4.2.4 Characterization ..........................................................................................................................183
  4.3. RESULTS AND DISCUSSION ..................................................................................................................185
  4.4. CONCLUSIONS .......................................................................................................................................196
  4.5. REFERENCES ..........................................................................................................................................197

Chapter 5.  Epoxy and Hydroxy Functional Polyolefin Macromonomers ...........................................................................198
  5.1. SYNOPSIS ...............................................................................................................................................198
  5.2. INTRODUCTION .......................................................................................................................................198
    5.2.1 Thermodynamic Miscibility of Blends ...........................................................................................199
List of Figures:

Chapter 2

Figure 2-1. Aqueous Dispersion Prepregging ..................................................5

Figure 2-2. Polymer Stabilization By Steric and Electrostatic Mechanisms .................................................................9

Figure 2-3. S\text{N}Ar Mechanism ............................................................................15

Figure 2-4. Benzyne Elimination-Addition Mechanism .......................................19

Figure 2-5. S\text{RN}1 Mechanism with Carbon-Oxygen Bond Formation ..............20

Figure 2-6. Apparatus for Polymerization of Poly(arylene ether)s ....................24

Figure 2-7. Resonance and Inductive Effects on pKa of Pyridine Ether ...............26

Figure 2-8. pH Value Effect on Protonation of Pyridine ......................................27

Figure 2-9. Hydrolysis of Poly(ether ether ketimine-co-ether ether pyridine) ........30

Figure 2-10. Synthesis of Poly(ether ether ketimine-co-ether ether pyridine) .........31

Figure 2-11. Reactivity Study of 2,6-Dichloropyridine with Monophenolate ......46

Figure 2-12. $^1$H NMR of Reaction Mixture from 2,6-Dichloropyridine Reactivity Study at 1 Minute .................................................................48

Figure 2-13. $^1$H NMR of Reaction Mixture from 2,6-Dichloropyridine Reactivity Study at 120 Minutes .................................................................49

Figure 2-14. Mole Fraction of Reactants as a Function of Time .........................51

Figure 2-15. Kinetic Expression for Complex Second Order Reactions ..........52

Figure 2-16. Second Order Kinetic Plot to Determine $k_1$ for Model Reaction .................................................................54

Figure 2-17. Second Order Kinetic Plot to Determine $k_2$ for Model Reaction ....55
Figure 2-18. Reactivity of 2,6-Dichloropyridine...............................57

Figure 2-19. ¹H NMR of Product of Reaction of 2 moles Hydroquinone
Monophenolate with 1 mole 2,6-Dichloropyridine..........................62

Figure 2-20. Reaction of 2 Moles Hydroquinone with 1 Mole 2,6-
Dichloropyridine..............................................................................63

Figure 2-21. Synthesis of 2,6-Bis(4-hydroxyphenyl ether) pyridine..........65

Figure 2-22. ¹H NMR of Benzyl Protected 2,6-Bis(4-hydroxyphenyl
ether) pyridine ...............................................................................66

Figure 2-23. ¹H NMR of 2,6-Bis(4-hydroxyphenyl ether) pyridine ..........67

Figure 2-24. Polymerization Scheme of Pyridine containing Poly(arylene
ether)s..............................................................................................71

Figure 2-25. Dynamic Thermal Gravimetry Traces for Pyridine
Containing Poly(arylene ether)s..........................................................74

Figure 2-26. Size Exclusion Chromatography Trace of P(EEP-co-EES)
with LMW Component.......................................................................78

Figure 2-27. Transesterification Mechanism in Pyridine Containing
Poly(arylene ether)s.........................................................................82

Figure 2-28. ¹³C NMR of P(EEP-co-EESO) Pyridine Containing
Poly(arylene ether)...........................................................................84

Figure 2-29. ¹³C NMR of P(EEP-co-EEK) Pyridine Containing
Poly(arylene ether)...........................................................................85

Chapter 3

Figure 3-1. Synthesis of Controlled <Mₙ> Ultem™ Type Poly(amic acid)......93

Figure 3-2. Imide Chemical Structure..................................................95

Figure 3-3. Polymerization of 4-Aminophthalic Anhydride.....................96

Figure 3-4. Two-step synthesis of Polyimide.........................................98

Figure 3-5. Mechanism for Amine Reacting with Anhydride to form Amic
Acid..................................................................................................99
Figure 3-6. Interfacial Type Polymerization in Diffusion Range of Dianhydride Particle ................................................................. 106

Figure 3-7. Anhydride Peak Height as Function of Temperature During Poly(amic acid) Imidization ................................................................. 108

Figure 3-8. Reactions Occuring During Imidization of Poly(amic acid) ........ 109

Figure 3-9. Thermal Conversion of Isoimide to Imide ............................................. 110

Figure 3-10. Ultem™ Type Polyimide Tg = 220°C ........................................... 116

Figure 3-11. Ultem™ Type Poly(amic acid) to Poly(amic acid) Salt to Polyimide .................................................................................. 117

Figure 3-12. Influence of Mole % Base to -COOH on Stability of Aqueous Triethylammonium Poly(amic acid) Salt Solutions ................. 119

Figure 3-13. Viscosity chromatogram of (a) ODPA/ODA polyamic acid and (b) oxadiphthalic anhydride/diaminodiphenylsulfone (ODPA/DDS) polyimide .................................................................................. 124

Figure 3-14. Apparatus for Collection of Poly(amic acid) Salt Imidization Volatiles .................................................................................. 135

Figure 3-15. Molecular weights of Ultem poly(amic acid) (Monitoring progress of the reactions over time) ...................................................... 140

Figure 3-16. Size Exclusion Chromatography Traces of Poly(amic acid) Synthesized in THF and NMP ........................................................................... 142

Figure 3-17. SEC results for Ultem™ type Poly(amic acid) polymerized in THF .................................................................................. 144

Figure 3-18. Comparison of Theoretical vs. Empirical <Mn> Increase with Time (Experimental Values Without LMW Component) ............... 147

Figure 3-19 and 3-20. Photographs of Polyimidies Prepared from Poly(amic acid) Salts .................................................................................. 155

Figure 3-21 and 3-22. Photographs of Polyimidies Prepared from Poly(amic acid) Salts .................................................................................. 156

Figure 3-23. Tg vs. 1/<Mn> for Polyimidies from Poly(amic acid) Salts ....... 160
Chapter 4

Figure 4-1. Poly(ether ether ketone) (PEEK) ................................................................. 178

Figure 4-2. Therminol VP1 ............................................................................................ 180

Figure 4-3. Therminol 75 ............................................................................................ 180

Figure 4-4. Triton X-100 stabilizer .............................................................................. 184

Figure 4-5. Synthesis of PEEK-ketimine precursor, and hydrolysis to PEEK ................................................................. 187

Figure 4-6. Formation of PEEK Particles in a High Temperature Solvent ........... 188

Figure 4-7. Scanning transmission electron micrographs of PEEK particles (20,000 X mag) ......................................................................................... 190

Figure 4-8. Scanning transmission electron micrographs of PEEK particles (70,000 X mag) ......................................................................................... 191

Figure 4-9. Atomic force micrograph of a PEEK particle aggregate ..................... 192

Chapter 5

Figure 5-1. Preparation of Epoxy Terminated Polyolefin Macromers .............. 211

Figure 5-2. $^1$H NMR of Si-H terminated Poly(butadiene) .................................... 213

Figure 5-3. Hydrogenation of Si-H Terminated Polydiene to Polyolefin ............ 216

Figure 5-4. $^1$H NMR of Epoxy Terminated and Dihydroxy Terminated Polyolefins ................................................................................................. 218

Figure 5-5. Preparation of Dihydroxy Functional Polyolefin Macromers .......... 219

Figure 5-6. Poly(ester-g-olefin) Copolymerization ................................................. 223

Figure 5-7 Poly(ester-g-olefin) Copolymer Formation by GPC .......................... 224
List of Tables

Table 2-1. Structure of Pyridine Containing Poly(arylene ether)s..........................38
Table 2-2. Kinetic Data from 2,6-Dichloropyridine Reactivity Study .........................50
Table 2-3. Properties of Pyridine Containing Poly(arylene ether)s..........................73
Table 2-4. Comparison of Tg of Containing Poly(arylene ether)s with Bisphenol-A Containing Poly(arylene ether)s.................................................................76
Table 2-5. GC-MS of LMW Component in Pyridine Containing Poly(arylene ether)s.................................................................79
Table 3-1. Results of Calculation of Stoichiometry for 20,000 g/mole PAA.................................................................104
Table 3-2. Poly(amic acid) Salt Preparation..............................................................133
Table 3-3. Solubilities of Poly(amic acid) Salts ......................................................151
Table 3-4. Hydrated Ionic Diameters Calculated from Ionic Mobilities.......................152
Table 3-5. Wt. Loss on Imidization, and Thermal Properties of Polyimides from Poly(amic acid) Salts .................................................................154
Table 3-6. Molecular Weights of Polyimides from Poly(amic acid) Salts......................158
Table 3-7. Potentiometric Titration of Imidized Poly(amic acid) Salts with HBr for Aromatic -NH2 .................................................................161
Table 3-8. Chain Relaxing During Imidization of Poly(amic acid) Salts.......................164
Table 3-9. Species detected by GC-MS Analysis of Imidization Products ..........167
Table 4-1. GC-Mass Spectrometry Analysis of PEEK Purification .........................193
Table 4-2. Thermal Properties of PEEK Before and after Particle Formation ..........195
Table 5-1. Molecular Weight and Microstructure of Si-H Functional Poly(butadiene) Oligomers.................................................................214
Table 5-2. Epoxy Group Ring Opening on the Polyolefin Macromonomers.................220
Table 5-3. Probability Distributions For Reaction Of 2 Moles Macromonomer With 1 Mole Diester.................................................................230
Chapter 1 - Scope of Dissertation

The research presented in this dissertation is comprised of two distinctly separate areas, of which Chapters 2 through 4 comprise the first area, and Chapter 5 comprises the second.

The first major area is concerned with production of carbon fiber-polymer matrix composites, utilizing aqueous processes. In Chapter 2, the synthesis and characterization of a series of pyridine containing poly(arylene ether)s useful as electrostatic stabilizers for aqueous dispersion prepregging are detailed. In Chapter 3, a study exploring the production of controlled molecular weight distribution poly(ether-imide)s via poly(amic acid) salts is reported. Water soluble poly(amic acid) salts, capable of producing controlled molecular weight polyimides, would be ideal for sizing carbon fibers, or for use in aqueous dispersion prepregging as electrostatic/steric stabilizers. In Chapter 4, a scaled up method of precipitating and purifying sub μm poly(ether ether ketone) particles from a high temperature organic solvent is related. These small PEEK particles are potentially useful as composite matrix forming materials by the aqueous dispersion prepregging process.

In the second area addressed by this dissertation, the synthesis of macromers useful in the field of polyester-polyolefin blend compatibilizers is addressed. In Chapter 5 the synthesis of epoxy functional and dihydroxy functional macromonomers and use in the preparation of polyester-polyolefin graft copolymers is described.
Chapter 2 Pyridine Containing Poly(arylene ether)s

2.1. SYNOPSIS

Thermoplastic particles stabilized by aqueous suspension stabilizers can be impregnated into carbon fiber tow and subsequently consolidated into fiber reinforced, thermoplastic matrix composites. This chapter describes the design of thermally stable pyridine containing poly(arylene ether)s to adsorb onto thermoplastic particles and, when converted to the pyridinium salts, electrostatically stabilize aqueous suspensions of the particles.

In a previous study by Brink et. al, poly(ether ether pyridine-co-ether ether ketone) was synthesized using hydroquinone, 2,6-dichloropyridine and 4,4'-difluoro-N-benzohydroxyldene aniline monomers reacted under nucleophilic aromatic substitution conditions. Up to 30 mole % pyridine groups were incorporated into copolymers which were used to stabilize poly(ether ether ketone) (PEEK) particles in aqueous solutions. In order to obtain high molecular weight materials using 2,6-dichloropyridine as a monomer, conditions for these polymerizations had to be altered relative to those employed for other polymerizations by this mechanism. It was necessary to add the 2,6-dichloropyridine subsequent to complete dehydration of the phenolic groups. Secondly, relatively long reaction times were required (≈ 35 hours at 160°C). These factors made high or controlled molecular weights difficult to achieve when more than approximately 30 mole % pyridine relative to ketimine monomer was incorporated into the polymers.

This study presents an alternative method for the synthesis of pyridine ether containing polymers which circumvents these factors. This chapter will first describe a reactivity study of 2,6-dichloropyridine which reveals wide
reactivity differences between nucleophilic attack to remove the first chlorine relative to reaction of the second chlorine. The synthesis of a novel pyridine containing bisphenol monomer (2,6-bis(4-hydroxyphenyl ether)) will be discussed in detail. Next the synthesis, characterization and some properties of a series of copolymers incorporating 2,6-bis(4-hydroxyphenyl ether) and dihalides of varying chemical composition will be described. The novel pyridine containing bisphenol monomer, 2,6-(p-hydroxyphenoxy)pyridine, was prepared and used for the synthesis of a series of poly(arylene ether)s containing sulfone, sulfoxide, phosphine oxide, ketimine, and ketone moieties.

2.2. INTRODUCTION

2.2.1 Thermoplastic Carbon Fiber Composites From Fine Particles

Polymer-fiber composites are important materials for applications where high strength/weight ratios are required. Thermoset matrix materials such as epoxy resins have been used predominantly for aerospace applications in combination with graphite fibers. High performance thermoplastic polymers have potential advantages in comparison to thermoset materials, such as indefinite shelf life, excellent strength and lifetime at elevated temperatures, and the possibility of reprocessing thermoplastic composites. When manufacturing a composite, it is desirable to first coat the fibers with a matrix material to form a "prepreg". The prepreg is "laid up" into the desired form, and is then processed into the composite with heat and pressure. Manufacturing "prepregs" from the melt is usually undesirable due to high melt viscosities leading to poor wetting, and also due to chemical degradation occurring at melt temperatures. Prepregging from solution is problematic in that the high performance
thermoplastics are typically only soluble in acidic or toxic high boiling solvents. Because of these factors, prepregging from thermoplastic powders is currently being studied \(^2\text{-}^6\). Two main methods are being developed. One method is based on using a dry powder in an electrostatic fluidized bed deposition process. Development of this method at V.P.I. has been described recently\(^4\). The second type of process, "Aqueous Dispersion Prepregging", is a wet method utilizing water as the medium in which the thermoplastic particles are dispersed (Figure 2-1). This aqueous dispersion requires some method for preventing flocculation or coagulation of the thermoplastic particles (stabilization), especially for cases where the thermoplastic particles are approaching colloidal dimensions (\( \leq 1 \, \mu \text{m} \) diameter). Recent work has also focused on the importance of the composition at the interphase, and the possibility for improving overall composite properties by adding an interphase modifier during processing \(^7\). The objective in this research has been to synthesize polymeric stabilizers which will 1) adsorb onto thermoplastic particles and 2) enable stable aqueous dispersions of these particles to be prepared for the purpose of aqueous dispersion prepregging. Here at V.P.I., one of the composite systems being prepared by aqueous dispersion prepregging is poly(ether ether ketone) (PEEK)/carbon fiber \(^3,^5,^6,^8\). In this effort to design, synthesize and utilize polymeric stabilizers for aqueous dispersion prepregging the focus is accordingly on the PEEK/carbon fiber system. Additional requirements for the polymeric stabilizers are 3) high thermal stability, 4), no low molecular weight by-product when consolidating the composite, and 5), suitable mechanical properties for the carbon fiber-PEEK matrix interphase region. Other properties are also desirable, including
Figure 2-1. Aqueous Dispersion Prepregging
miscibility with the PEEK matrix.

2.2.2 Nature of the Approach

The first part of this approach is to design and synthesize thermally stable pyridinium containing poly(arylene ether)s which can act as electrostatic stabilizers for PEEK particles in water. These stabilizers do not necessarily have to be water soluble or dispersible to act as electrostatic stabilizers, but it is a secondary objective to design and synthesize water soluble/dispersible high performance polymer systems by gaining an understanding of the structure-property relationships in largely aromatic polyelectrolyte systems.

The second part of this approach will be discussed in Chapter 3, and is to synthesize Ultem™ type polyimide poly(amic acid) precursors and neutralize these precursors with organic bases, such as tetraethylammonium hydroxide, or triethylamine under mild conditions that will avoid hydrolysis of the main chain amide linkage. Following formation of the prepreg, the poly(amic acid) salt will be cyclized to the polyimide with evolution of the gaseous decomposition products from the organic counterion (prior to consolidation).

2.2.3 Stabilization of Colloidal Dispersions

Colloidal dispersions consist of a dispersion medium (the continuous phase), and a dispersed phase with particles ≈ 0.001 μm to ≈ 1 μm in diameter. When a dispersion is made up of particles greater than ≈ 1 μm in diameter, it is said to be a suspension. Colloidal dispersions have unique properties owing to the high surface area to volume ratio of the dispersed phase. The free energy required to form a surface is equal to the surface free energy multiplied by the newly formed area. Conversely, when colloidal particles coagulate, the
process is thermodynamically spontaneous due to the decrease in free energy of the system. Particles in colloidal dispersions may aggregate by either coagulation or flocculation. Coagulation is an irreversible aggregation process where the particles are driven tightly together. Flocculation is a reversible aggregation process where the particles are joined loosely to form a porous floc. The primary attractive forces between colloidal particles are van der Waals attractions of a primarily induced dipole - induced dipole nature, or London Forces. The Hamaker constant $A$ is used to quantify the London attractive forces between two particles, and is a function of temperature and distance between the particles. The same electronic oscillations causing optical dispersion are responsible for the London "dispersion" forces. The Hamaker constant $A$ can be evaluated for a substance macroscopically by complex calculations utilizing the optical and dielectric properties of the material. For two spheres of radius $a$, the van der Waals attraction ($V_A$) is

$$V_A = -\left(\frac{A^*}{6}\right)G$$

where $A^*$ is the Hamaker constant, and $G$ is a geometric term which is a function of the particle radius, and the minimum distance of separation between the particles. Typical values of Hamaker constants for single materials range from about $10^{-19}$J to $10^{-20}$J.

The thermal energy available to the particles at 20°C is ~ 1.5 kT. This energy is not sufficient in magnitude to overcome the van der Waals attractive forces and prevent aggregation of a colloidal dispersion. Therefore, in order to stabilize a colloidal dispersion, a repulsive energy barrier must be introduced (by placing a stabilizer at the particles' surface) which will be greater in magnitude than the van der Waals energy of attraction. This repulsive energy
barrier can be imparted by an electrostatic mechanism or a steric mechanism (Figure 2-2).

2.2.3.1 Electrostatic Stabilization
For an electrostatic mechanism to be operative, like charges are placed on the particle surfaces which, in aqueous media, typically give rise to a diffuse double layer. It is the Coulombic repulsion between the diffuse double layers which imparts electrostatic stabilization over relatively long distances.

2.2.3.2 Steric Stabilization
Steric stabilization is typically imparted by attaching macromolecules (adsorption or grafting) to the particle surfaces\textsuperscript{9}. For the steric mechanism to work properly, the polymer should be soluble or dispersible in the liquid dispersion medium. As two particles approach closely enough for the attached polymer chains to interact, or interdigitate, a steric repulsion results due to the decrease in entropy of the system upon interdigitation. Steric stabilization can also be explained in terms of the repulsive force caused by osmotic diffusion of solvent into the region of increased polymer concentration \textsuperscript{11}. However, it is to be noted that in contrast to electrostatic stabilization, there are no long range repulsive forces. For the steric mechanism to work efficiently, the polymer should not exceed a certain molecular weight. High molecular weight polymer can adsorb onto two or more particles simultaneously, resulting in bridging flocculation. The most efficient polymeric steric stabilizers are typically block or graft copolymers with one soluble component, and one insoluble component.
POLYMERIC STABILIZATION

Figure 2-2. Polymeric stabilization: a) Steric stabilization; b) Electrostatic stabilization; c) Combination of steric and electrostatic stabilization
which acts as an "anchor" block. It is noted that combinations of electrostatic and steric stabilization mechanisms are also possible.

In this project, we were interested in stabilizing aqueous dispersions of thermoplastic particles. A suitable steric stabilizer should be water soluble, or water dispersible. Water soluble polymers have two main categories, nonionic polymers and polyelectrolytes. Nonionic water soluble polymers (i.e.; poly(ethylene oxide), polyvinylalcohol) are typically materials of low thermal stability, and are thus unsuitable for composite applications, unless they are to be removed prior to consolidation. For this reason, we were interested in thermally stable polyelectrolyte systems to be utilized as electrostatic and / or steric stabilizers.

2.2.3.3 Polyelectrolytes

Polyelectrolytes are polymers with many ionizable groups. Polyelectrolytes can be classified as anionic, cationic or ampholytic, depending on the nature of the charges on the ionized polymer. The repulsion of charged groups on a polyelectrolyte result in expanded conformations for ionized polyelectrolytes and require careful consideration when determining the molecular weights of polyelectrolytes in solution. The conformations are dependent on the solution's electrolyte content. High concentrations of electrolyte in the solution will decrease the size of the diffuse double layer surrounding the polyelectrolyte charges, decreasing repulsions and leading to smaller chain conformations.

"Counterion condensation" is a well known phenomenon encountered with polyelectrolytes. According to theory, in a dilute solution of polyelectrolytes in water at 20°C, the counterions are completely dissociated
from the macroions if the average distance between charges is 7Å or greater. When the average distance between charges becomes less than 7Å, the counterions in the solution begin to "condense" onto the polyelectrolyte chain in order to shield the ions bound to the chain from the repulsive charge between neighboring like ions. At an average distance of 7Å the electrostatic attractive energy is \( = kT \). This implies that the maximum charge density, and thereby maximum interaction with the aqueous medium can be achieved when the average distance between charges is 7Å or less \(^{13}\). Decreasing the polyelectrolyte charge spacing distance below \( = 7Å \) will not increase the charge density, since the attractive electrostatic force binds counterions very strongly.

Wholly aromatic polyelectrolytes are by and large uncommon materials. It is difficult to predict the solubility of these polymers in water a priori using molar attraction constants of functional groups to calculate solubility parameters \(^{14}\). Quantitative theories have been developed for determining the radius of gyration, and second virial coefficient for polyelectrolytes in dilute solution by combining existing theories of electrostatic interactions with theories of worm like chains, but these theories have not yet been applied to wholly aromatic polyelectrolytes \(^{15}\). These types of materials should have excellent thermal stability. It is not yet known what types of mechanical properties they will possess, but the potential for processing these high performance polymers from water is exciting.
2.2.4 Structure-Property Relationships in Poly(Arylene Ether)s

Poly(arylene ether)s are a diverse group of engineering plastics with varied properties, depending upon the composition of the specific poly(arylene ether). The glass transition temperature is one parameter affecting the mechanical properties at the range of use temperatures for a poly(arylene ether). The presence or absence of crystallinity is also very important in determining mechanical properties at temperatures above the Tg, and also the solvent resistance. The properties of the polymers can often be correlated directly to the structures of the polymers. For example, increasing the number of ether-linkages per repeat unit will tend to lower the Tg, along with improving the solubility. Incorporating meta linked phenylene groups in the poly(arylene ether) will tend to disrupt the crystalline order as compared to the corresponding para linked moieties. Functional groups present in the poly(arylene ether)s can impact both the intermolecular and intramolecular forces of interaction in the bulk polymer, and will correspondingly affect the mechanical properties.

2.2.5 Polymerization Mechanisms Of Poly(Arylene Ether)s

2.2.5.1 Electrophilic Aromatic Substitution

Functional groups in poly(arylene ether)s play a key role during their synthesis, depending upon the reaction mechanism. There are two major routes for polymerization of poly(arylene ether)s\textsuperscript{16}. These are electrophilic aromatic substitution, and nucleophilic aromatic substitution.

One early preparation for such materials utilizing the electrophilic mechanism is the reaction of isophthaloyl or terephthaloyl chloride with diphenyl ether in a Friedel-Crafts acylation reaction using AlCl\textsubscript{3} as a catalyst.
Using this route, large excesses of AlCl₃ are required along with a Lewis base such as DMF to produce high molecular weight polymers. These same monomers can be polymerized in liquid HF using BF₃ as the catalyst. A more recent example of the use of electrophilic aromatic substitution to produce a wholly aromatic polyketone (or poly(ether ketone)) utilizes the reaction of 2,2'-dimethoxybiphenyl with an ether containing diacid chloride in 1,2-dichloroethane at 20°C using anhydrous AlCl₃ as the catalyst. Medium to high molecular weights were achieved using this method.

2.2.5.2 Scholl Reaction

Another synthetic route to prepare aromatic polyethers containing ketone or sulfone functionalities will be mentioned briefly. The so-called Scholl reaction, involves the cation-radical polymerization of bis(aryl-oxy) derivatives by carbon-carbon bond formation. This method has been recently developed by Percec and colleagues. The Scholl reaction utilizes FeCl₃ as the oxidant in a nitrobenzene solvent.

2.2.5.3 Nucleophilic Aromatic Substitution

This section will focus on nucleophilic aromatic substitution routes to poly(arylene ether)s. To date this has proven to be the most convenient and most widely utilized route to prepare poly(arylene ether)s. An activated dihalide monomer is reacted with a bisphenolate, formed from a bisphenol in situ by reaction with potassium carbonate, or preformed by reaction with an exact equivalence of potassium or sodium hydroxide. In general, a dipolar aprotic solvent such as 1-methyl-2-pyrrolidinone (NMP), N,N-dimethylacetamide (DMAc), or dimethylpropyleneurea (DMPU), is used as the solvent. Diphenylsulfone or benzophenone are used in cases where high reaction
temperatures (> 200 °C) are required. In this nucleophilic route, the reactivity of the dihalide monomer depends upon both the electron withdrawing ability of activating groups, and also on the identity of the halide. The strength of the electron withdrawing groups as pertaining to the reactivity of the dihalide monomer decreases in the order NO₂ ≈ SO₂ > C=O > N≡N. The halide substituent reactivities decrease with F >> Cl > Br > I. The bisphenate’s reactivities decrease according to the metal counterion present, with Cs > K > Na > Li. The reasons for these relationships will be discussed in the next section. Non-traditional activating groups such as heterocyclic rings and the azino group have also been reported to successfully activate aryl fluorides.

2.2.5.4 S_NAr (Addition - Elimination Mechanism)

The S_NAr mechanism for nucleophilic substitution on aromatic compounds is well known. It is also known as the addition-elimination reaction, which for the synthesis of arylene ethers denotes the addition of the phenolate, then elimination of the halide. A nucleophile attacks an electron deficient carbon bonded to a halogen substituent on an aromatic ring. The carbon is electron deficient both due to the resonance withdrawing ability of an ortho or para situated electron withdrawing group, and also due to the inductive withdrawing effect of the halogen substituent. A delocalized carbanion complex called a "Meisenheimer Intermediate" forms, and this formation is the rate limiting step for the reaction (Figure 2-3).
Figure 2-3. SNAr Mechanism
The electron withdrawing activating group typically plays a key role in accepting a large part of this negative charge density and stabilizes the Meisenheimer complex, thus lowering the activation energy of the $S_{N}Ar$ reaction, and increasing its rate. Another key factor in determining the rate of the $S_{N}Ar$ reaction is the electronegativity of the halogen. Since formation of the Meisenheimer is the rate limiting step, the electron inductive ability of the halogen plays an important role in monomer reactivity. Therefore, as described above, the reactivity decreases in the order, F $\gg$ Cl $\gg$ Br $\gg$ I which parallels the decreasing electronegativity of the halogen substituent. The last step in the $S_{N}Ar$ reaction is departure of the halogen ion. For the case where a potassium phenolate is utilized as the nucleophile, the halogen ion will combine with the potassium cation and form a solid precipitate in the reaction medium. This precipitation of the reaction product will help to drive the reaction to completion.

2.2.5.5 Benzyne Mechanism

The benzyne nucleophilic aromatic substitution mechanism (or the elimination-addition mechanism) is much less important than the $S_{N}Ar$ mechanism for the production of poly(arylene ether)s, but it will be discussed briefly. A strong base may abstract the relatively acidic protons ortho to a halogen substituent on an aryl halide \(^{21}\). Next the anion formed by the proton abstraction eliminates the halide ion, producing the highly unstable, and highly reactive benzyne species. The benzyne bond is formed from the somewhat poorly overlapping sp\(^2\) orbitals on two adjacent carbons. The rate determining step is in some cases the proton abstraction, in which case fluorine has highest reactivity, or the rate determining step may be loss of halide ion, in which case the rate order is I $\gg$ Br $\gg$ Cl $\gg$ F. A
nucleophile can quickly add to the benzyne bond at either carbon of the benzyne bond site, producing an anion complex which can abstract a proton to form the product (Figure 2-4). Note that the benzyne reaction produces an isomeric product mixture, and that this mechanism does not occur readily at lower temperatures ($\leq 200^\circ C$).

2.2.5.6 Single Electron Transfer or $SN_1$

Aromatic substitution on an aryl halide may occur via the $SN_1$ reaction, the main feature of which is a single electron transfer. The main feature of the $SN_1$ mechanism is an electron transfer between the nucleophile and the aryl halide 22. This is a free radical type chain mechanism, involving an initiation, propagation, and a termination step. The reactions are often initiated by light, which accelerates the initiation step. The $SN_1$ mechanism is shown in Figure 2-5 for the reaction of phenolate with 4-chlorobenzophenone to form an arylene ether. No direct evidence of the propagation step (3) in Figure 2-5 to form an oxygen-carbon bond has been observed in the literature. 2,6-Dichloropyridine and other dihalobenzenes have been shown to be reactive towards $SN_1$ type reactions under certain conditions 23,24. For example, 2,6-dichloropyridine was reacted with an excess of the potassium enolate of pinacolone in liquid anhydrous ammonia, and was irradiated with a strong light source, forming an 86% yield of the disubstituted product with no monosubstituted product detected 24. In this case, carbon-carbon bonds are formed between the dichloropyridine, and the pinacolone. Phenolates are among the nucleophiles that participate in $SN_1$ type reactions 25-27. For example phenoxide may react with 4-bromobenzophenone in liquid ammonia or dimethylsulfoxide, by using electrochemical catalysis to form carbon coupling products exclusively 26. For
the reaction of phenolates with aryl halides, coupling by the $\text{SnAr}$ mechanism has not been found to occur through a carbon oxygen bond, but rather through a carbon-carbon bond $^{25-27}$. However, it should be noted that the conditions used to induce the $\text{SnAr}$ reaction in low molecular weight compounds, such as liquid ammonia solvents, and UV irradiation, or electrochemical catalysis, do not reflect the conditions used to synthesize high molecular weight poly(arylene ether)s.

2.2.5.7 Reductive Dehalogenation vs. Substitution in Polyetherification of Bis(aryl chloride)s

Percec and coworkers have studied the conditions which cause reductive dehalogenation to occur when synthesizing poly(arylene ether)s $^{28-31}$. In 1991 Percec et al. published a study which discussed results of experiments reacting keto activated bisarylchlorides or keto activated bisarylfuorides with bisphenoxides under typical conditions for $\text{SnAr}^{28,29}$. The polymers made from the difluorides were in all cases higher molecular weight than the corresponding polymers made with the dichloride monomers. The polymerization reactions of the difluorides were complete in about 10 hours, while by contrast, about 25 hours were required to react the dichloride monomers under the same conditions. The use of t-butyl hydroquinone resulted in lower molecular weights for the dichloride monomers as compared to Bisphenol A, with the bis(aryl chloride) monomers, but not with the bis(aryl fluoride) monomers $^{28,29}$. Percec et al. found that in the case of the low molecular weight polymers that a benzophenone unreactive endgroup was detectable by $^1$H NMR. This indicated that an $\text{SnAr}$ type initiation mechanism was participating, where the halide containing phenyl ring was reduced through
Step 1: Benzyne Formation

Step 2: Phenolate Attack

Product is mixture of isomers from A + B routes.

(B product)

Figure 2-4. Benzyne Elimination-Addition Mechanism
Initiation (1)

\[
\text{Ph-C-Cl} + e^- \rightarrow \text{Ph-C-}^-\text{Cl}
\]

Propagation

(2)

\[
\text{Ph-C-}^+\text{Cl}^- \rightarrow \text{Ph-C}^+ + \text{Cl}^-
\]

(3)

\[
\text{Ph-C-}^+ + \text{Ph-O}^- \rightarrow \text{Ph-C-Ph-O}^-
\]

(4)

\[
\text{Ph-C-Ph-O}^- + \text{Cl-Ph-C}^- \rightarrow \text{Ph-C-Ph-O}^- + \text{Cl-Ph-C}^-
\]

Termination (5)

\[
\text{Ph-C-}^+ + \text{H} \rightarrow \text{Ph-C-H}
\]

Figure 2-5. SRN1 Mechanism with Carbon-Oxygen Bond Formation
a single electron gain, and that subsequently the chloride ion departed. The free radical benzophenone moiety then abstracted a hydrogen atom to form the benzophenone unreactive endgroup observed by NMR. Thus, evidence was provided that steps (1), (2) and (5) in Figure 2-5 were occurring, particularly for the bis(arylchloride) monomers, resulting in lower molecular weight polymers through a reductive elimination of chlorine from the chain ends. Percec presented the possibility that the $SR\underline{\underline{N}}$1 mechanism might also compete with the $SNAr$ mechanism in the propagation of the polymer.

In a subsequent communication, Percec explained the results noted above using the hard and soft acid and base semi-empirical principle. Percec proposed that the $SNAr$ reaction is the preferred route for hard bases and hard acids, such as the Bisphenol A phenolate hard base reacting with the bis-(aryl fluoride) hard acid to form a poly(arylene ether). He also proposed that a soft acid soft base pair, would tend to be more likely to react by the single electron transfer pathway leading to reductive elimination at the chain ends. An example of a soft base soft acid pair of reactants is the sterically hindered tert-butyl hydroquinone reacted with a bis(aryl chloride) such as 4,4'-dichlorobenzophenone. In this case, lower molecular weight poly(arylene ether) will result.

In Percec's more recent publication, synthesis of poly(arylene ether ketone)s with the purpose of expanding on the previous work, and elucidating the factors governing the selectivity between $SNAr$ and reductive dehalogenation. In the lower molecular weight polymers synthesized, the carbon-carbon link was not observed by NMR experiments. Percec deduced
that propagation was not occurring by the SRN1 mechanism in view of the fact that carbon-carbon bonds were not detected by NMR. The reactivity differences between hydroquinones and Bisphenol A are explained by the fact that hydroquinones are stronger electron donors, and have higher oxidation potentials than Bisphenol A, resulting in more reductive halogenation for hydroquinone by the single electron transfer mechanism. The reactivity toward single electron transfer as related to the halogen group, increases in the order F < Cl < Br < I, as the corresponding substrates are more easily reduced. Solvent was found to be a factor in the occurrence of reductive dehalogenation, DMAc did not appear to promote reductive dehalogenation, but NMP did. The single reductive dehalogenation reactions were more prevalent for higher reaction temperatures.

Other recent studies have used phase transfer catalysts to increase the rates of polymerization of dihalide monomers with aromatic diphenols reacted by S_NAr mechanisms. These studies showed that polymers made by this method had faster reaction rates, and reached higher molecular weights than the analogous polymer prepared using longer times without the phase transfer catalyst. The author suggested that the single electron transfer mechanism leading to lower molecular weight is less important in these cases, due to shorter reaction times. The fluoride ion on the phase transfer catalyst did not cause nucleophilic cleavage at high temperatures, as had been observed previously.

In summary, certain combinations of monomers, when reacted by S_NAr type mechanisms utilizing an activated bishalide, and a bisphenolate, encounter a single electron transfer reaction, that can result in elimination of
functionality from that moiety of the poly(arylene ether), resulting in low molecular weights. This mechanism occurs particularly readily with dichlorobenzophenone or dibromobenzophenone during reaction with hydroquinone phenolate. The dichlorobenzophenone is relatively readily reduced compared to some other activated dihalides, and the hydroquinone is readily oxidized. By utilizing difluoride monomers, and DMAc as solvent and avoiding hydroquinone when possible, higher molecular weight poly(arylene ether)s can be made. By using rate increasing phase transfer catalyst systems, higher molecular weight poly(arylene ether)s can be achieved from bis(aryl chloride)s. It is possible that the SR\textsubscript{N}1 mechanism does compete with the SNAr mechanism in the propagation of the polymer in forming carbon-oxygen bonds, but this propagation forming carbon-oxygen by SR\textsubscript{N}1 can not be readily detected, as the end result is exactly the same as by the SNAr mechanism.

2.2.5.8 Use of Potassium Carbonate to Form a Phenolate In Situ

One method for synthesis of poly(arylene ether)s that has seen wide application in recent years is the reaction of activated dihalide monomers with bisphenols in dipolar aprotic amide solvents in the presence of a small excess of potassium carbonate and a toluene azeotrope to remove the water by-product of the reaction. The phenolate ions are formed in situ. A typical apparatus used for this polymerization includes a Dean-Stark trap which collects the water by-product of the reaction (Figure 2-6). This method can be preferable to the use of strong bases such as sodium or potassium hydroxide, as slight excesses of K\textsubscript{2}CO\textsubscript{3} may be used without hydrolysis of halide groups by the excess base. The kinetics of this reaction was studied by Viswanathan et al., in DMAc\textsuperscript{34}. Deviation from simple second order kinetics was noted and
Figure 2-6. Apparatus for Polymerization of Poly(arylene ether)s
attributed to the partially heterogeneous nature of the potassium carbonate during the reaction. In a subsequent study involving the polymerization of wholly aromatic polysulfones, it was found that N-methyl-2-pyrrolidone was preferable as a solvent for the polymerization as the higher boiling point under atmospheric pressure (bp 250°C/740mm) allowed for higher reaction temperatures and increased the solubility of the bisphenate intermediates in comparison to DMAc or dimethylsulfoxide (DMSO). In another study it was found that deactivated monomer systems (activated dihalides with less active bisphenols or halogenophenols) that could not be polymerized to high molecular weight poly(arylene ether)s in NMP, could be readily polymerized to high molecular weights using diphenylsulfone as the solvent at temperatures up to 320°C.

2.2.6 Pyridine Containing Polymers as Polyelectrolytes

Pyridine containing polymers can be converted to ion containing polymers if the pyridine moiety is protonated by an acid (or quaternized by alkylation). The pK_a of pyridine has been determined to be 5.15. The pK_a of a pyridine ether, such as that found in pyridine containing poly(arylene ether)s, will be affected in two ways by the oxygen atoms in the ortho positions (Figure 2-7). The resonance effect donating electrons from the oxygens to the nitrogen should increase the pK_a value. The electron inductive withdrawing effect of the oxygens should decrease the pK_a value. The two effects might be mutually cancelling, resulting in a pK_a similar to pyridine. The polyelectrolytic activity of a pyridine moiety containing polymer is pH dependent. By combining the equations for the pK_a of pyridine with the equation for pH, a relationship is established for the ratio of protonated pyridine to non-protonated pyridine, as a
Figure 2-7. Resonance and Inductive Effects on $\text{pK}_a$ of Pyridine Ether
1) \[
\begin{align*}
&\text{H}^+ + \text{H}_2\text{O} \rightleftharpoons \text{N} \quad \text{+ H}_3\text{O}^+ \quad (\text{pKa} = 5.15) \\
&\begin{array}{c}
\text{N} \\
\text{H}_2\text{O} \\
\text{H}_3\text{O}^+
\end{array}
\end{align*}
\]

2) \[\text{pKa} = -\log \left[ \frac{[\text{H}_3\text{O}^+]}{[\text{H}^+]} \right] \]

3) \[\text{pH} = -\log [\text{H}_3\text{O}^+] \]

4) \[
\begin{array}{c}
\text{N} \\
\text{H}_2\text{O} \\
\text{H}_3\text{O}^+
\end{array}
\]

\[
\begin{array}{c|cccc|cc}
\text{pH} & 2 & 3 & 4 & 5 & 6 & 7 \\
\hline
\text{10}^{(\text{pKa-pH})} & 1400 & 140 & 14 & 1.4 & 0.14 & 0.014 \\
\% \text{H}^+ & 99.9 & 99.3 & 93 & 67 & 12 & 1.4
\end{array}
\]

Figure 2-8. pH Value Effect on Protonation of Pyridine
function of pH (Figure 2-8). For dilute aqueous solutions of pyridine at pH values of 5, ~67% of the pyridine molecules will be protonated. At a pH of 4, ~93% of the pyridine molecules are protonated. Thus, at lower pH's in aqueous solution, pyridine containing polymers can become cationic polyelectrolytes.

Another method of forming a polyelectrolyte from pyridine containing polymers is via quaternization of the pyridine moiety with an alkylating reagent. Poly(vinylpyridine)s have been quaternized by a vapor phase reaction with alkyl halides such as methyl bromide with a resultant improvement in mechanical properties due to an increase in $T_g$ [39]. The N-alkyl (quaternary) derivatives of both poly(4-vinylpyridine) and poly(2-vinylpyridine) have been shown to exhibit strong polyelectrolyte behavior [40].

Kricheldorf and coworkers synthesized and characterized a series of pyridine containing poly(arylene ether)s as possible semi-permeable membrane materials [38,41,42]. Poly(pyridine ether)s were prepared by the bulk condensation of 2,6-dichloro- or 2,6-difluoropyridine with silylated diphenols [41] and also by solution polymerization of the same reagents in N-methyl-2-pyrrolidone in the presence of potassium carbonate [42]. Using 2,6-dichloropyridine high molecular weights could not be obtained, so the more expensive 2,6-difluoropyridine was primarily utilized [41,42]. Solution characterization results suggested that these poly(pyridine ether)s assumed highly coiled conformations in methylene chloride, and less tightly coiled conformations in methylene chloride with added trifluoroacetic acid [41,42].

In a subsequent paper, Kricheldorf and colleagues quaternized aromatic poly(pyridine ether)s using six different alkylating agents under varying
conditions in deuterated solvents and analyzed the reactions by $^1$H NMR \textsuperscript{38}. Nitrobenzene proved to be the most useful solvent. Methyl triflate, and dimethylsulfate were the most reactive alkylating species. This high reactivity is apparently neccessary, as the poly(pyridine ether)s are sterically hindered in the 2,6 positions \textsuperscript{38}. Dimethylsulfate was used for preparative quaternization since it was commercially available. None of the quaternized poly(pyridine ether)s were completely soluble in hot water, but in some cases gelation was observed \textsuperscript{38}. It is noted that the smallest repeat unit in this polymer series was = 10Å in length. It is possible that further decreasing the repeat unit length to $\leq$ 7Å would render quaternary poly(pyridine ether)s water soluble. The ionic pyridine containing poly(arylene ether)s which exhibited crystallinity by DSC measurement did not form gels.

Another method of synthesizing a wholly aromatic ion containing poly(arylene ether) is by sulfonation of the pre-polymerized poly(arylene ether). For example, Johnson et al. detailed the synthetic route and characterization methods for the commercially important sulfonated bisphenol-A polysulfone which is used as a membrane for water desalination \textsuperscript{43}. A 2:1 complex of SO$_3$ and triethyl phosphate, as developed by Noshay and Robeson \textsuperscript{44}, was added to the polysulfone which was predissolved in 1,2-dichloroethylene. The reaction proceeded quickly at room temperature, and addition of sodium hydroxide to the reaction mixture yielded the sodium salt product \textsuperscript{43}. The sulfonated bisphenol-A polysulfone materials absorbed up to 45% water by weight at 70°C, but were not water soluble.

In a previous study poly(ether ether pyridine-co-ether ether ketone) was synthesized using hydroquinone, 2,6-dichloropyridine and 4,4'-difluoro-N-
benzhydroxylidene aniline monomers reacted under nucleophilic aromatic substitution conditions. Up to 30 mole % pyridine groups were incorporated into a copolymer which was used to stabilize poly(ether ether ketone) (PEEK) particles in aqueous solution in hydrolyzed form (Figure 2-9). Using this approach, however, it was necessary to add the dichloropyridine subsequent to complete dehydration of the phenolic groups in order to achieve high or controlled molecular weights. Secondly, relatively long reaction times were required (≈35 hours at 160°C). These factors made high or controlled molecular weights difficult to achieve when more than approximately 30 mole % pyridine relative to ketimine was incorporated into the polymers (Figure 2-10).

Figure 2-9. Hydrolysis of Poly(ether ether ketimine-co- ether ether pyridine).
Figure 2-10. Synthesis of Poly(ether ether ketimine-co-ether ether pyridine)
with up to 30 mole % (ether ether pyridine)
The poly(ether ether pyridine-co-ether ether ketimine) with a molar ratio of pyridine to ketimine of 30/70 was studied by Xie et al. to define the parameters for its use in electrostatically stabilizing PEEK particle dispersions. Adsorption of the ketimine containing copolymer onto the PEEK particles was essentially nonexistent from tetrahydrofuran, but efficient adsorption occurred from toluene (> 50% adsorption at 1 wt. % stabilizer relative to particles). Following hydrolysis to the ketone functionality, the copolymer stabilized aqueous suspensions of 12 μm diameter PEEK particles. Submicron diameter particles flocculated quickly under the same conditions. It was speculated that water soluble steric stabilizers should have greater efficiency in stabilizing the submicron particles.

2.3. EXPERIMENTAL

2.3.1 Materials:

4,4'-Difluorobenzophenone was kindly supplied by ICI Inc. and was purified by recrystallization from absolute ethanol followed by drying under reduced pressure at 45°C overnight (mp 102-105°C).

Toluene (EM Science) was purified by washing with sulfuric acid, followed by distillation from sodium under nitrogen (bp 110.6°C).

N,N-Dimethylacetamide (DMAc) purchased from Fisher, was purified by stirring over calcium hydride under nitrogen followed by distillation from calcium hydride under reduced pressure. The DMAc was stored in a septum sealed bottle under Argon until use (bp 164.5-166°C).
Potassium Carbonate was ground with a mortar and pestle, and then dried at 130°C at reduced pressure for 24 hours.

Potassium Hydroxide was purchased from Mallinckrodt (87.8 %) and used as received.
Hydroquinone (99+%) was purchased from Aldrich and used as received (mp 172-175°C).

2,6-Dichloropyridine (Aldrich) was recrystallized from absolute ethanol, and then dried at room temperature under reduced pressure (86-88.5°C).

4-(Benzylxoy)phenol (Aldrich 98%) was used as received (mp 120-122°C).

4-tert-Butylphenol (Aldrich 98%) was purified by sublimation from an 80°C bath (mp 98-101°C).

4,4'-Difluoro-N-benzohydroxylideneaniline, the ketimine monomer, was synthesized and purified as previously reported (mp 114-115 °C).

Bis(4-chlorophenyl)sulfone (Aldrich 98%) was purified by recrystallization from toluene (mp 145-148°C).

Bis(4-fluorophenyl)phenyl phosphine oxide was synthesized and purified as previously reported (mp 124-126°C)°.

33
**Bis(4-fluorophenyl)sulfoxide** was synthesized and purified as previously reported (m.p. 51.0-51.5°)\(^4\).

*The purities of the monomers were checked by measuring their melting points at a heating rate of 1 °C/min using a Mel Temp capillary melting point apparatus.*

**2.3.2 Model Study**

2,6-Dichloropyridine (1.665 g, 0.01125 mole) was added to 4-tert-butylphenol (3.381 g, 0.02251 mole) in 30 mL DMAC at 160°C which had been dehydrated to phenolate in-situ with potassium carbonate (2.331 g, 0.01687 mole) with water removed via toluene azeotrope. Samples of 0.25 mL were periodically removed, and immediately diluted with 0.50 mL of deuterated chloroform to quench the reaction. These samples were filtered and placed in a 5 mm NMR tube for \(^1\)H NMR analysis.

**2.3.3 Monomer Synthesis (2-Chloro-6-(4-hydroxyphenyl ether) pyridine)**

\[
\text{HO} \quad \overset{O}{\text{N}} \quad \overset{\text{Cl}}{\text{Cl}}
\]

The following is a procedure used to synthesize the A-B type monomer (2-Chloro-6-(4-hydroxyphenyl ether)pyridine). Hydroquinone, (10.00 grams, 0.09082 mole) was placed in 125 mL of toluene in a 250 mL 2 necked flask equipped with magnetic stirring, a Dean Stark Trap with cold water condenser, and a slow argon flow. To this reactor was added 0.95 mole % potassium
hydroxide (Assay 87.8 % KOH), or 5.500 grams (0.09082 mole). The reactants were refluxed for 20 hours. About 1 mL of the aqueous phase was collected in the Dean Stark Trap. After cooling to room temperature, the product was recovered by vacuum filtration on a Büchner funnel, washed with 250 mL of near boiling toluene, and quickly transferred to a tared 100 mL round bottom flask, sealed with a septum and evacuated. The product was heated at 90°C on a vacuum line (= 1 mm Hg) for 20 hours to remove residual toluene. After cooling to room temperature, the sealed flask with product was charged with a positive pressure of Argon, and stored without exposure to light. The potassium hydroquinone phenolate was always used within 3 days of preparation.

A 1.1 molar excess of potassium hydroquinone phenolate (9.59 grams, 0.0647 mole) was placed into a flame dried 250 mL 3-necked round bottomed flask equipped with a thermocouple, reflux condenser, and argon inlet. Next, 2,6-dichloropyridine (8.62 grams, 0.0582 mole) and 125 mL of dimethylsulfoxide were added to the reactor. The reactor was sealed, and the reaction contents were heated to 80 °C for 24 hours with stirring, and slow argon flow. Next, the reactor was cooled to room temperature, and a precipitate formed. The precipitate was collected by vacuum filtration, washed well with water, and air dried. Upon characterizing the product of the reaction by 1H NMR it was discovered that some of the desired product formed, but that an undesirable side product also formed in significant amounts. This will be further discussed in the Results and Discussion section. Yield of 2-chloro-6-(4-hydroxyphenyl ether)pyridine in the reaction mixture was ≈ 50 mole % by 1H NMR.
2.3.4 Monomer Synthesis (2,6-Bis(4-hydroxyphenyl ether) pyridine)

The following is the three step procedure for the synthesis of 2,6-bis(4-hydroxyphenyl ether) pyridine. In the first step 4-(benzyloxy)phenol (100.0 g, 0.4994 mole) was placed in a two-neck 1000 mL flask equipped with magnetic stirring, Dean Stark Trap, condenser, and Argon inlet. Toluene (400 mL) was added as an azeotroping agent, followed by potassium hydroxide (0.4744 mole, 30.25 g) with an assay of 88%. The reaction mixture was heated to reflux and maintained for a minimum of 3 hours. After cooling the reaction mixture to room temperature, the 4-(benzyloxy)phenolate was collected by vacuum filtration and washed with 800 mL of near boiling toluene to obtain an off-white crystalline product. The 4-(benzyloxy)phenolate was dried under reduced pressure at 50°C.

In the second step the 4-(benzyloxy)phenolate was dissolved in DMAc (500 mL) with gentle heating. After cooling, 2,6-dichloropyridine (31.22 g, 0.2110 mole) dissolved in 125 mL DMAc was added. The reaction mixture was stirred at room temperature for 48 hours. The monoadduct was judged to be quantitatively formed by 1H NMR. The reaction mixture was raised to 80°C and maintained for 72 hours. After cooling, the benzyl protected product was precipitated into methanol/water (75/25) and washed with water until the wash liquid was "water white", and dried under reduced pressure at 60°C.
In the third step, the benzyl protected product (94.2 grams, 0.198 mole), glacial acetic acid (500 mL) and concentrated hydrochloric acid (200 mL) were placed in a 2000 mL flask equipped with a magnetic stir bar, condenser, and argon inlet. The reactants were heated at 80°C for 48 hours. After cooling, the thick reaction mixture was diluted with 3000 mL water and stirred. After the product settled, the supernatant liquid was removed by siphon. This wash was repeated 8 times. The product 2,6-bis(4-hydroxyphenyl ether) pyridine was dried for 48 hours under reduced pressure at 60°C prior to purification. Yield of unpurified 2,6-bis(4-hydroxyphenyl ether) pyridine was = 100 %.

2.3.5 2,6-Bis(4-hydroxyphenyl ether) Pyridine Purification

The crude 2,6-bis(4-hydroxyphenyl ether) pyridine (15g, 0.051 mole) was dissolved in ethanol and passed through a neutral alumina column. The ethanol was evaporated to obtain white crystals. The crystals were washed with chloroform, collected by vacuum filtration, and dried in the vacuum oven at 60 °C for 24 hours. The 2,6-bis(4-hydroxyphenyl ether) pyridine was recrystallized by dissolving it in a minimum of boiling ethanol, and then adding small aliquouts of boiling water until a small amount of precipitation occurred, and then adding a small amount of additional ethanol to produce a homogeneous solution. After the solution was allowed to cool slowly to room temperature, white, needle-like crystals formed. The recrystallized 2,6-bis(4-hydroxyphenyl ether) pyridine was collected by vacuum filtration, washed with a room temperature ethanol/water mixture (50 mL/50 mL) and dried at 60°C under reduced pressure. The chloroform wash and recrystallization followed by drying were repeated a second time. The product was characterized by 1H and
Table 2-1. Structure of Pyridine Containing Poly(arylene ether)s and Acronyms Used

Poly (ether ether pyridine-co-ether ether ketone) \( P(\text{EEP-co-EEK}) \)

Poly (ether ether pyridine-co-ether ether ketimine) \( P(\text{EEP-co-EEKt}) \)

Poly (ether ether pyridine-co-ether ether sulfoxide) \( P(\text{EEP-co-EESO}) \)

Poly (ether ether pyridine-co-ether ether sulfone) \( P(\text{EEP-co-EESO}_2) \)

Poly (ether ether pyridine-co-ether ether phenyl phosphine oxide) \( P(\text{EEP-co-EEPPO}) \)
13C NMR, and by direct injection mass spectrometry. The product was also analyzed by elemental analysis for chlorine.

2.3.6 Synthesis of Pyridine Containing Poly(arylene ether)s

The syntheses of poly(ether ether pyridine-co-ether ether ketone) (P(EEP-co-EEK)), poly(ether ether pyridine-co-ether ether ketimine) (P(EEP-co-EEKt)), poly(ether ether pyridine-co-ether ether sulfoxide) (P(EEP-co-EESO)), poly(ether ether pyridine-co-ether ether sulfone) (P(EEP-co-EESO2)), poly(ether ether pyridine-co-ether ether phenyl phosphine oxide) (P(EEP-co-EEPO)) were carried out via nucleophilic aromatic substitution reactions in a dipolar aprotic solvent (DMAc), using uncontrolled molecular weight conditions (1:1 monomer stoichiometry). Yields for all polymers were = 100% of theoretical. The structures of the pyridine containing poly(arylene ether)s and their abbreviated names are shown in Table 2-1.

Synthesis of P(EEP-co-EEK) in DMAc

Purified 2,6-bis(4-hydroxyphenyl ether) pyridine (5.0200 grams, 0.1700 mole), purified 4,4'-difluorobenzophenone (3.7094 grams, 0.1700 mole) and sodium carbonate (1.982 grams, 0.0187 mole) were dissolved in 25 mL of DMAc in a three-neck 100 mL round bottom flask equipped with an overhead mechanical stirrer, a Dean Stark trap, a condenser, an argon inlet and a thermocouple. Toluene (25 mL) was added to the polymerization solution as an azeotroping agent. The reaction mixture was heated at 140°C for 3 hours with a moderate argon flow to dehydrate the system but no water was collected in the Dean Stark trap. The reaction temperature was raised to 160°C by simultaneously increasing the temperature of the oil bath and removing a small
amount of toluene from the Dean Stark trap. Following 1.5 hours at 160°C with no water production, an additional 0.72 gram (0.00679 mole) of sodium carbonate was added. Almost immediately, water began to collect in the Dean Stark Trap. Once the reaction temperature reached 155°C, the reaction was allowed to stir for 19 hours with a slow argon flow. After 12 hours the reaction mixture was very viscous. The solution was cooled to room temperature and precipitated into water in a Waring blender, collected by vacuum filtration, washed with additional water and dried under reduced pressure at 60°C. To further purify the P(EEP-co-EEK), 4 grams were dissolved in 60 mL NMP at 150°C, and then precipitated into a 3:1 mixture of methanol and water which was rapidly stirring in a Waring blender. The small particles collected were washed three times with 100 mL of water, and were then dried under reduced pressure at 80°C for 48 hours. P(EEP-co-EEK) was soluble in DMSO, DMAc and NMP at high temperatures (= 150°C).

**Synthesis of P(EEP-co-EEKt) Pyridine Containing Poly(arylene ether)**

Purified 2,6-bis(4-hydroxyphenyl ether) pyridine (7.1158 grams, 0.024097 mole), purified 4,4'-difluoro (N-benzohydroxylidene aniline (7.0684 grams, 0.024098 mole) and potassium carbonate (5.0088 grams, 0.03624 mole) were dissolved in 80 mL of DMAc in a four-neck 250 mL round bottom flask equipped with an overhead mechanical stirrer, a Dean Stark trap, a condenser, a nitrogen inlet and a thermocouple. Toluene (50 mL) was added to the solution as an azeotroping agent. The reaction mixture was heated at 140 °C for 4 hours with moderate argon flow to dehydrate the system, and then the temperature was raised to 160°C by simultaneously increasing the temperature.
of the oil bath and removing some toluene from the Dean Stark trap. Once the reaction temperature reached 160°C, the reaction was allowed to stir for 20 hours with a slow argon flow. The solution was then cooled to room temperature and diluted with 40 mL DMAC. The copolymer was precipitated into water, collected by vacuum filtration, washed with additional water and dried under reduced pressure at 60°C for 48 hours.

The syntheses of P(EEP-co-EESO), P(EEP-co-EESO₂) and P(EEP-co-EEPO) were conducted using the same general procedure as detailed above for P(EEP-co-EEKt).

The quantities of reagents used are as follows:

**Synthesis of P(EEP-co-EESO) Pyridine Containing Poly(arylene ether)**

- 2,6-bis(4-hydroxyphenyl ether) pyridine; 7.0400 grams, (0.023841 mole)
- Bis(4-fluorophenyl)sulfoxide, 5.6800 grams (0.023841 mole)
- Potassium Carbonate, 4.96 grams (0.0359 mole)
- DMAC, 80 mL. Toluene, 50 mL.

**Synthesis of P(EEP-co-EESO₂) Pyridine Containing Poly(arylene ether)**

- 2,6-bis(4-hydroxyphenyl ether) pyridine; 7.0003 grams, (0.023706 mole)
- Bis(4-chlorophenyl)sulfone, 6.8076 grams (0.023706 mole)
- Potassium Carbonate, 4.92 grams (0.0356 mole)
- DMAC, 80 mL. Toluene, 50 mL.

41
Synthesis of P(EEP-co-EEPPO) Pyridine Containing Poly(arylene ether)

2,6-bis(4-hydroxyphenyl ether) pyridine; 6.9284 grams, (0.023463 mole)
Bis(4-fluorophenyl)phenyl phosphine oxide, 7.3737 grams (0.023463 mole)
Potassium Carbonate, 5.01 grams (0.0363 mole)
DMAc, 80 mL. Toluene, 50 mL.

Solubility of P(EEP-co-EKt), P(EEP-co-EESO), P(EEP-co-EESO2) and P(EEP-co-EEPPO)

The four pyridine containing poly(arylene ether)s were soluble in DMAc, NMP, DMSO, chloroform, and tetrahydrofuran.

2.3.7 Second Precipitation of the Pyridine Containing Poly(arylene ether)s

For each pyridine containing poly(arylene ether), [with the exception of the insoluble P(EEP-co-EK)], 2.0 grams of the polymer were dissolved in 40 mL of chloroform. This solution was precipitated into 500 mL of methanol stirring rapidly in a Waring blender. The polymer precipitates were collected by vacuum filtration, and were dried under reduced pressure overnight at 60°C. The precipitation solvent was evaporated using a rotary evaporator. The resultant white crystalline solid residue remaining upon evaporation of the precipitation solvent was analyzed by mass spectroscopy and gel permeation chromatography.
2.3.8 Dispersion of Pyridine Containing Poly(arylene ether)s in Water

[For P(EEP-co-EEKt), P(EEP-co-EESO), P(EEP-co-EESO₂) and P(EEP-co-EEPPO)]

(1) Pyridine containing poly(arylene ether) was dissolved in tetrahydrofuran (THF) (0.1 gram in 2 mL) and was precipitated into 15 mL 0.01 M HCl (pH = 2.3).

(2) HCl (1.0 M) was added dropwise to THF solution of polymer (0.1 gram in 2 mL) until precipitation occurred.

(3) Pyridine containing poly(arylene ether) 0.5 gram (= 1 E-3 mole) was dissolved in 10 mL of THF. To this solution was added a stoichiometric amount of 1.0 M HCl (8.2 mL of concentrated HCl diluted to 100 mL with THF). To this solution, water was added slowly with rapid stirring, until precipitation occurred.

None of above methods resulted in stable aqueous dispersions of the pyridine containing poly(arylene ether)s. In all cases, gross phase separation occurred.

2.3.9 Characterization of Pyridine containing Copolymers

Gel Permeation Chromatography

Molecular weight distributions for copolymers were determined on a Waters Gel Permeation Chromatograph using a chloroform mobile phase with a flow rate of 1 mL / min at 30 °C, relative to polystyrene standards. μ-Styrage HT columns were used with pore sizes of 10⁴ and 10³ Å.

Intrinsic Viscosities

Solution viscosity measurements were carried out in chloroform at 25 °C.
Nuclear Magnetic Resonance Spectrometry

$^1$H and $^{13}$C NMR analysis were performed on a Varian Unity NMR spectrometer operating at 400 MHz ($^1$H NMR).

Thermal Analysis

Thermal gravimetry (TG) was carried out on a Perkin-Elmer Series 7 Thermal Analyzer. Thermal data was obtained in air with a heating rate of 10 °C/min. Differential Scanning Calorimetry was conducted in nitrogen with a heating rate of 10°C/min on a Perkin Elmer DSC-2C.

Mass Spectrometry

Secondary Ion Mass Spectrometry of the low molecular weight components was carried out on a Fisons VG QUATTRO Mass Spectrometer, using a nitrobenzyl alcohol viscous liquid substrate, a cesium ion source and a direct injection technique.

2.4. RESULTS AND DISCUSSION

2.4.1 Model Study of Reactivity of 2,6-Dichloropyridine

In a previous study (Brink et al.\(^2\)) conducted by Riffle's group, poly(ether ether pyridine-co-ether ether ketone) was synthesized using hydroquinone, 2,6-dichloropyridine and 4,4'-difluoro-N-benzohydroxylidine aniline monomers reacted using nucleophilic aromatic substitution conditions. Up to 30 mole % pyridine groups were incorporated into these copolymers which were used to stabilize poly(ether ether ketone) (PEEK) particles in aqueous solutions in their hydrolyzed form (Figure 2-10). It was necessary to add the dichloropyridine subsequent to complete dehydration of the phenolic groups in order to achieve high or controlled molecular weights. Also, relatively long reaction times were
required (= 35 hours at 160°C). These factors made high or controlled molecular weights difficult to achieve when more than approximately 30 mole % pyridine relative to ketimine was incorporated into the polymers. Several reasons can be proposed to explain these results. The water formed during the phenolate formation may hydrolyze the 2,6-dichloropyridine before the water is removed azeotropically with toluene. The 2,6-dichloropyridine may undergo a single electron transfer mechanism leading to a chain termination step which limits the molecular weight when a high mole percent of 2,6-dichloropyridine is charged. The 2,6-dichloropyridine is reacting slowly at one or both of the chloride substituted positions.

In order to probe the cause of these results, the reactivity of 2,6-dichloropyridine toward nucleophilic aromatic substitution was investigated using a model study. The conditions of the model study approximated the polymerization conditions (Figure 2-11). tert-Butylphenol (a monofunctional phenol), was dehydrated using potassium carbonate in DMAc with a toluene azeotrope and a Dean Stark trap to remove the product of the dehydration, water, using an experimental apparatus similar to that shown in Figure 2-6. After the tert-butylphenolate was fully formed, as determined by ^1^H NMR, 2,6-dichloropyridine was added to the reactor at a ratio of one mole of 2,6-dichloropyridine per two moles of tert-butylphenolate. Small samples were taken as the reaction proceeded and were "quenched" to stop the reaction in deuterchloroform (CDCl\textsubscript{3}). The aliquots were analyzed by ^1^H NMR, and the analysis was repeated one day later (for the early times) to ensure that the composition of the aliquots had not changed due to further reaction in the deuterchloroform. The peaks observed by ^1^H NMR were assigned to the

45
Reaction of 2,6-Dichloropyridine (1 mole) with 4-tert-butylphenolate (2 mole)

A \( \text{(CH}_3\text{)}_3\text{C} - \text{O}^- \text{K}^+ \) + B \( \text{Cl}_2 \text{N} - \text{Cl} \) \[ \xrightarrow{k_1} \] C \( \text{(CH}_3\text{)}_3\text{C} - \text{O} \text{N} - \text{Cl} \) \( \text{Mono-adduct (MA)} \)

\( \text{(CH}_3\text{)}_3\text{C} - \text{O}^- \text{K}^+ \) + MA \( \xrightarrow{k_2} \) E \( \text{(CH}_3\text{)}_3\text{C} - \text{O} \text{N} - \text{O} \text{C} - \text{C}(\text{CH}_3\text{)}_3 \) \( \text{Di-adduct (DA)} \)

Rate Rxn 1 = \( k_1[\text{PA}][\text{DCP}] = d[\text{DCP}] / dt \)
Rate Rxn 2 = \( k_2[\text{PA}][\text{MA}] = d[\text{DA}] / dt \)

* Concentrations of reaction species determined on a Varian 400 MHz NMR by integrating meta proton peaks noted above.

Figure 2-11. Reactivity Study of 2,6-Dichloropyridine with Monophenolate
various species occurring during the reaction. The peaks corresponding to the protons meta to the nitrogen were well resolved, and the areas of these peaks were used to calculate the mole fraction and molarity of reactants (with the knowledge of the initial concentrations). In Figures 2-12 and 2-13 the $^1$H NMR assignments from the reaction mixture are shown for reaction times of 1 minute and 120 minutes. The integrated peak areas of the peaks of interest, the calculated reaction mixture concentrations, and the calculated rate constants are listed in Table 2-2. A discussion of how the rate constants were calculated follows.

Mole fractions of the pyridine containing chemical species occurring during the reaction are plotted as a function of time in Figure 2-14. For purposes of nomenclature, the product of the reaction of t-butylphenolate with dichloropyridine will be called the "monoadduct", while the product of the reaction of t-butylphenolate with the monoadduct will be called the "diadduct". Figure 2-14 shows that the t-butylphenolate reacts readily with the first chlorine on 2,6-dichloropyridine to form the monoadduct quantitatively within 60 minutes. The reaction forming the diadduct occurs much more slowly, with 24 hours required for quantitative diadduct formation. This type of reaction, where $A + B$ forms $C + D$, and subsequently $A + C$ forms $E + D$ is termed a complex second order reaction. The mathematical treatment of the kinetics is detailed in Pannetier and Souchay's Book “Chemical Kinetics” 47. The expression shown in Figure 2-15 may be used to solve for the rate constants $k_1$ and $k_2$ for this reaction. An iterative computer program may be used to solve for these values. A simpler method, considering that the 2,6-dichloropyridine is largely consumed before much diadduct has formed, allows one to treat both reactions separately,
Figure 2-12 $^1$H NMR of Reaction Mixture from 2,6-Dichloropyridine Reactivity Study at 1 Minute
Figure 2-13 $^1$H NMR of Reaction Mixture from 2,6-Dichloropyridine Reactivity Study at 120 Minute
Table 2-2. Kinetic Data From 2,6-Dichloropyridine Reactivity Study

<table>
<thead>
<tr>
<th>Actual Integral Area</th>
<th>Concentration (moles/liter)</th>
<th>time min.</th>
<th>time secs</th>
<th>( k_1 t )</th>
<th>( k_2 t^* )</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA</td>
<td>0.25</td>
<td>0.183</td>
<td>0.046</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>HB</td>
<td>0.067</td>
<td>0.2036</td>
<td>0.2193</td>
<td>0.061</td>
<td>0.00</td>
</tr>
<tr>
<td>HC</td>
<td>0.433</td>
<td>0.2964</td>
<td>0.2193</td>
<td>2.97</td>
<td>0.00</td>
</tr>
<tr>
<td>46.55</td>
<td>1</td>
<td>60</td>
<td>0.67</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.74</td>
<td>15</td>
<td>900</td>
<td>4.65</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.00</td>
<td>75</td>
<td>4500</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.00</td>
<td>120</td>
<td>7,200</td>
<td>0.58</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.00</td>
<td>180</td>
<td>10,800</td>
<td>1.31</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.00</td>
<td>240</td>
<td>14,400</td>
<td>2.23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.00</td>
<td>360</td>
<td>21,600</td>
<td>4.48</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.00</td>
<td>720</td>
<td>43,200</td>
<td>14.45</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.00</td>
<td>1440</td>
<td>86,400</td>
<td>0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[
k_1 t = \frac{1}{[PA]_0 - [DCP]_0} \ln \left[ \frac{[PA][DCP]_0}{[PA]_0[DCP]} \right] \quad k_2 t = \frac{1}{[PA]} - \frac{1}{[PA]_0}
\]

*For the calculation of \( k_2 \) \([PA]_0 \) was defined as 0.2193 M at 75 minutes.
Reaction of t-butyl phenolate (2 moles) with dichloropyridine (1mole) at 160°C in DMAc

Figure 2-14. Model Study: Mole Fraction of Reactants as a Function of Time
Kinetics for Complex Second Order Reactions

\[ PA + DCP \rightarrow MA + KCl \]
\[ PA + MA \rightarrow DA + KCl \]

For the case where both reactions are second order and \( [PA]_0 = 2*[DCP]_0 \)

Then:

\[
\frac{[PA]}{[PA]_0} = \left[ \frac{2\left(\frac{k_2}{k_1}\right) - 1}{2\left(\frac{k_2}{k_1}\right) - 2} \right] \times \left[ \frac{[DCP]}{[DCP]_0} \right] - \left[ \frac{1}{2\left(\frac{k_2}{k_1}\right) - 2} \right] \times \left( \left[ \frac{[DCP]}{[DCP]_0} \right]^{\frac{k_2}{k_1}} \right)
\]

Key:
PA = 4-tert-butylphenolate
DCP = 2,6-dichloropyridine
MA = monoadduct
DA = diadduct

Figure 2-15. Kinetic Expression for Complex Second Order Reactions\(^{47}\)
as simple second order kinetic cases, where A reacts with B and forms a product. For 0 minutes until 15 minutes, as an insignificant amount of diadduct has formed, the differential form of the second order rate expression may be used:

\[
\frac{-d[A]}{dt} = k[A][B] = k([A]_0 - x)([B]_0 - x)
\]

The integrated form of the same equation is:

\[
k_1t = \frac{1}{[A]_0 - [B]_0} \ln \frac{[A][B]_0}{[A]_0[B]}
\]

By plotting the right side of the expression versus time, one can solve for \(k_1\) (Figure 2-16). Similarly, one can solve for \(k_2\) by recognizing that at \(\geq 75\) minutes, a negligible concentration of 2,6-dichloropyridine remains. Also, after the 2,6-dichloropyridine is consumed, for the remainder of the reaction, the concentration of monoadduct will be equal to the concentration of t-butylphenolate. For this special case of second order kinetics where \([A] = [B]\), the differential form of the rate equation is:

\[
\frac{d[A]}{dt} = -k_2[A]^2
\]

The integrated form of the rate equation is:

\[
k_2t = \frac{1}{[A]} - \frac{1}{[A]_0}
\]
Second Order Kinetics Plot
t-Butylphenolate with 2,6-Dichloropyridine
(First 15 minutes for k1)

\[ y = 0.18072 + 4.9782e^{-3x} \quad R^2 = 0.994 \]
\[ k1 = 0.005 \, \text{L/mole-sec} \]

Figure 2-16. Second Order Kinetic Plot to Determine \( k_1 \) for Model Reaction of 2,6-Dichloropyridine with t-Butylphenolate
Second Order Kinetics Plot
t-Butylphenolate with 2,6-Dichloropyridine
(time ≥ 75 minutes for k2)

\[ y = -1.3385 + 2.6141 \times 10^{-4}x \quad R^2 = 0.990 \]

\[ k_2 = 0.00026 \text{ L/mole\cdot sec} \]

Figure 2-17. Second Order Kinetic Plot to Determine \( k_2 \) for Model Reaction of 2,6-Dichloropyridine with t-Butylphenolate
By plotting the right side of the equation versus time, one can solve for $k_2$ (Figure 2-17). The results of the model study are as follows: The rate constant for the reaction of the t-butylphenolate with the first available site on 2,6-dichloropyridine in N,N-dimethylacetamide at 160°C was determined to be $5 \times 10^{-3}$ L/mole\(\cdot\)sec. The rate constant for the reaction of the t-butylphenolate with the monoadduct formed by the first reaction is $2.6 \times 10^{-4}$ L/mole\(\cdot\)sec. The ratio of $k_1/k_2 = 20$. This shows that the rate of the first substitution of the phenolate with 2,6-dichloropyridine occurs significantly faster than the ensuing substitution. This reactivity difference may be theoretically explained by examining the resonance forms of the Meisenheimer intermediates for the first and the second addition (Figure 2-18). The Meisenheimer intermediate for the first addition is stabilized by the ability of the nitrogen to accept a negative charge, as well as by the inductive electron withdrawing ability of the adjacent second chlorine. Once the monoadduct forms, a resonance structure exists whereby the oxygen can donate a pair of electrons to the pyridine ring, resulting in a negative charge on the nitrogen. The existence of this resonance form indicates that a partial negative charge already exists on the nitrogen, resulting in a decreased ability of the nitrogen to accept a negative charge to stabilize the Meisenheimer intermediate for the second substitution. The absence of a second electron withdrawing chlorine also makes the second substitution Meisenheimer intermediate less stable relative to the intermediate from step one.

2.4.2 Monomer and Polymer Synthesis

In view of the results of the previous study in which copolymers were synthesized directly from 2,6-dichloropyridine\(^2\), and the results of the model
Figure 2-18. Reactivity of 2,6-Dichloropyridine
study, it was decided to design a pyridine containing monomer which would allow for an alternative route for incorporating the pyridine moiety into a poly(arylene ether), while bypassing the direct use of 2,6-dichloropyridine as a monomer. A well designed novel pyridine containing monomer could potentially also result in other advantages over the existing electrostatic stabilizer, poly(ether ether pyridine-co-ether ether ketimine) (with a molar ratio of pyridine to ketimine of 30/70). It was desirable to increase the mole % of pyridine so as to improve the efficiency of electrostatic stabilization by increasing the charge density on the protonated pyridine containing poly(arylene ether). It was also desired to attain wholly amorphous morphologies in contrast to the semi-crystalline morphologies obtained with between 0 mole % pyridine to 30 mole % pyridine for the hydrolyzed ketone of the poly(arylene ether)s². Several monomer structures were considered. It was decided to attempt to synthesize the A-B type and A-A type monomers which follow:

\[
\text{HO-} \begin{array}{c} \text{O} \\ \text{N} \end{array} \begin{array}{c} \text{Cl} \\ \text{Cl} \end{array} \begin{array}{c} \text{Cl} \\ \text{Cl} \end{array} \text{OH}
\]

A-B Type Monomer (2-Chloro-6-(4-hydroxyphenyl ether) pyridine)

\[
\text{HO-} \begin{array}{c} \text{O} \\ \text{N} \end{array} \begin{array}{c} \text{O} \\ \text{OH} \end{array} \begin{array}{c} \text{O} \\ \text{OH} \end{array} \text{OH}
\]

A-A Type Monomer (2,6-Bis(4-hydroxyphenyl ether) pyridine)
A literature search did not reveal any prior disclosures of these structures. Both monomers, when incorporated into a poly(arylene ether) should retain excellent thermal stability due to their wholly aromatic structures. The A-B type monomer would have several potential advantages. If it could be highly purified, the inherent perfect stoichiometry of an A-B type monomer would ensure high molecular weight polymers at high degrees of conversions. Also, a homopolymer synthesized from this A-B monomer would have a high pyridine content, allowing for the synthesis of a pyridine containing poly(arylene ether) with an extremely high charge density in the protonated form (approximate charge spacing = 7.5 Å). Kricheldorf and coworkers synthesized similar poly(arylene ether)s from 2,6-difluoropyridine with silylated aromatic diols, including silylated hydroquinone and resorcinol 41. These materials have promise as water dispersible materials when in the quaternized form 38. However, Kricheldorf’s method resulted in polymers with low to moderate inherent viscosities 38. One possible drawback to the A-B type monomer is that the carbon activated toward nucleophilic aromatic substitution by the electron withdrawing chlorine would have relatively low reactivity, in analogy to the monoadduct in the model study of 2,6-dichloropyridine reactivity.

The A-A monomer (2,6-bis(4-hydroxyphenyl ether) pyridine) was of interest for preparing pyridine containing poly(arylene ether)s for several reasons. When reacted with difluorobenzophenone to form a poly(ether ether pyridine)\textsubscript{x}(ether ether ketone)\textsubscript{y} type copolymer, the mole % of (ether ether pyridine) could easily be varied by using a second bisphenol. However, in terms of charge spacing, the minimum charge spacing would be relatively large (20-25 Å). In terms of reactivity, 2,6-bis(4-hydroxyphenyl ether) pyridine
could be reacted in its phenolate form with a variety of activated dihalides. An interesting question is presented as to the effect incorporation of the 2,6-bis(4-hydroxyphenyl ether) pyridine monomer will have on the poly(arylene ether)'s morphology. Poly(ether ether ketone) has an extremely short lamellar thickness of only two repeat units, or \( = 30 \text{ Å} \). If a copolymer contains runs of (ether ether ketone) units of 2 or more, poly(ether ether ketone) crystallization can occur. In one study by scientists at ICI, copolyarylene ethers were synthesized by two methods producing an alternating copolymer and a random copolymer, both having the same compositions of poly(ether sulfone)\(_x\)(ether ketone ketone)\(_y\). In the random copolymer, crystallinity resulted due to short runs of crystallizable (ether ketone ketone) units, while in the alternating copolymer with the same units but in a non-adjacent fashion, no crystallinity was detected. In the poly(ether ether pyridine)\(_x\)(ether ether ketone)\(_y\) type polymers synthesized previously by Brink et. al, crystallinity was detected by differential scanning calorimetry at up to 30 mole % (ether ether pyridine). No crystallinity was observed in the same copolymers in their ketimine form, so the crystallinity was apparently due to runs of adjacent (ether ether ketone) units. If a copolymer of 2,6-bis(4-hydroxyphenyl ether) pyridine and 4,4'-difluorobenzophenone was completely alternating, crystallinity might not occur. However, if a random copolymer was produced via a transesterification mechanism, crystallinity would likely result. The absence of crystallinity could result in pyridine containing poly(arylene ether)s with improved solubility.
2.4.3 Synthesis of 2-Chloro-6-(4-hydroxyphenyl ether) pyridine

\[
\begin{align*}
\text{HO} &\quad \text{O} \\
&\quad \text{N} \\
&\quad \text{Cl}
\end{align*}
\]

An attempt was made to synthesize 2-chloro-6-(4-hydroxyphenyl ether) pyridine, an A-B type monomer, using a slight excess of the mono potassium phenolate of hydroquinone reacted with 2,6-dichloropyridine in dimethylsulfoxide. The $^1$H NMR of the product mixture is shown in Figure 2-19. The reaction did not yield solely the desired product. Once 2-chloro-6-(4-hydroxyphenyl ether) pyridine (the substitution product of one hydroquinone phenolate with one 2,6-dichloropyridine) is formed in the reaction, a proton was abstracted by a molecule of potassium hydroquinone phenolate. The resulting more stable phenolate then reacted with 2,6-dichloropyridine to form the unwanted dichloride byproduct (Figure 2-20). The dihalide byproduct and the desired product were formed in approximately a 1:1 molar ratio. The two products were not readily separated, so this route was abandoned. However, the information gained in the attempt was useful, as the knowledge of the proton exchange when using potassium hydroquinone phenolate influenced the decision to utilize benzyl protected hydroquinone phenolate as the nucleophile for the synthesis of the A-A type monomer, 2,6-bis(4-hydroxyphenyl ether) pyridine.
Figure 2.19. 1H NMR of Product of Reaction: 2 Mole Hydroquinone with 1 Mole 2,6-Dichloropyridine
Figure 2-20 Reaction of 2 Mole Hydroquinone with 1 Mole 2,6-Dichloropyridine
2.4.4 Synthesis of (2,6-Bis(4-hydroxyphenyl ether) pyridine)

Because of the rapid exchange that occurs between the hydroquinone phenolate and the first substitution product, it was decided to utilize a protected form of hydroquinone as the nucleophile. Benzyl protected hydroquinone, or 4-(benzyloxy)phenol was used as the nucleophile. 2,6-Bis(4-hydroxyphenyl ether) pyridine is formed through reaction of 2,6-dichloropyridine with 2 equivalents of the benzyl protected phenolate of hydroquinone and subsequent deprotection (Figure 2-21). After the 4-(benzyloxy)phenolate was prepared, it was reacted with 2,6-dichloropyridine in DMAc at 20°C. At this low temperature, the monoadduct quantitatively formed, with no substitution occurring at the remaining available activated site. Next the reaction temperature was raised to 80°C. At 80°C, substitution at the second site occurred quantitatively within 72 hours. Such long reaction times may not be required for quantitative conversion, but reaction times were not optimized, and the long times did not result in deleterious effects on the synthesis. The $^1$H NMR of the benzyl protected monomer is shown in Figure 2-22. The benzyl groups were removed by treatment with hydrochloric acid in acetic acid for 48 hours at 80°C. Immediately following the deprotection, the 2,6-bis(4-hydroxyphenyl ether) pyridine was in the hydrochloride salt form. Following deprotection, the crude monomer was washed copiously with water. Elemental chlorine analysis proved the absence of chloride ions in the product, establishing that the washed
Figure 2-21. Synthesis of 2,6-Bis(4-hydroxyphenyl ether) pyridine
Figure 2-22. $^1$H NMR of Benzyl Protected 2,6-Bis(4-hydroxyphenyl ether) pyridine
Figure 2-23. 1H NMR of 2,6-Bis(4-hydroxyphenyl) pyridine (Following Deprotection)
monomer was in the free base form, and not in the form of the hydrochloride. GC-Mass Spectrometry following the first recrystallization from ethanol/water showed that trace amounts of mono-benzyl protected 2,6-Bis(4-hydroxyphenyl ether) pyridine and benzyl chloride remained in the crude monomer. A second chloroform wash followed by a second recrystallization removed most of the residual impurities. The $^1$H NMR spectrum of 2,6-bis(4-hydroxyphenyl ether) pyridine is shown in Figure 2-23. The melting point of the purified 2,6-bis(4-hydroxyphenyl ether) pyridine was 212.3 - 212.7 °C.

2.4.5 Synthesis of Pyridine Containing Poly(arylene ether)s

It was desirable to incorporate 2,6-bis(4-hydroxyphenyl ether) pyridine into a series of pyridine containing poly(arylene ether)s by nucleophilic aromatic substitution polymerization reactions with various activated dihalide monomers. It was of interest to study the morphologies, thermal stabilities, sequence distributions, and aqueous dispersibilities of the resultant poly(arylene ether) series. Five activated dihalide monomers were investigated, which were known to impart distinctive properties to poly(arylene ether)s:

![4,4'-Difluorobenzophenone](image)

4,4'-Difluorobenzophenone
The 4,4'-difluorobenzophenone monomer imparted crystallinity to a poly(arylene ether) when random sequences existed, or when high mole percentages were incorporated, due to the polar nature and high symmetry of the ketone group. 4,4'-difluoro-N-benzohydroxylideneaniline was used to form
soluble and amorphous ketimine precursors, which could be hydrolyzed to ketone containing polymers, resulting in semi-crystalline poly(arylene ether)s in certain cases \(^{50-52}\). Bis(4-chlorophenyl)sulfone typically produces polymers with excellent thermal stabilities. The sulfone moiety itself does not impart crystallinity to a poly(arylene ether). Incorporation of bis(4-fluorophenyl)phenyl phosphine oxide is known for giving self-extinguishing characteristics to poly(arylene ether)s, and produces high char yields when these phosphorus containing poly(arylene ether)s are burned in air \(^{45}\). Bis(4-fluorophenyl)sulfoxide forms amorphous poly(arylene ether sulfoxides)s when reacted with hydroquinone or 4,4'-biphenol by nucleophilic aromatic substitution. The poly(arylene ether) sulfoxides could be reduced to crystalline poly(arylene ether sulfide)s with excellent thermal stability \(^{53}\).

The pyridine containing poly(arylene ether)s were synthesized as shown in Figure 2-24. Several comments should be made about the polymerization procedure. An apparatus identical to that shown in Figure 2-6 was used. The dihalide monomer was reacted with the 2,6-bis(4-hydroxyphenyl ether) pyridine monomer in a 1:1 stoichiometric ratio. If close to exact 1:1 stoichiometry is achieved, and the polymerization reaches high conversions, high molecular weight polymer is expected. The limiting factors on achieving high molecular weight are 1) monomer purity 2) accuracy of measurement 3) extent of reaction 4) absence of side reactions and 5) solubility of high molecular weight polymer in the reaction solvent. A 1.5 molar excess of K\(_2\)CO\(_3\) was used. It has been shown that excess K\(_2\)CO\(_3\) can be successfully used to form the phenolate in-situ, without having a deleterious effect on the molecular weight, as compared to the case of using a strong base.
HO-\text{O}_N\text{O}_N\text{O}_N\text{OH} + X-\text{Y}-\text{Y}-\text{X} \rightarrow \text{Polymer}

X = \text{Cl or F}

140^\circ \text{C for 3h}
160^\circ \text{C for 20h}

Dimethylacetamide / Toluene
1.5 mole excess K_2\text{CO}_3
(Na_2\text{CO}_3 for Y = carbonyl)

\begin{align*}
\text{Y} &= -\text{C}-, -\text{C}-, -\text{S}-, \\
&\quad -\text{SO}_2-, -\text{PO}_4-
\end{align*}

Figure 2-24. Polymerization Scheme of Pyridine containing Poly(arylene ether)s using 2,6-Bis(4-hydroxyphenyl ether) pyridine and Activated Dihalides
such as sodium or potassium hydroxide\textsuperscript{34}. Other researchers have found that a large excess does increase the initial polymerization rate, but that after continued heating, the molecular weight drops quickly and significantly \textsuperscript{54}. In future experiments it may be desirable to use a 1.05 molar excess of $K_2CO_3$, and limit the reaction times. This point will be discussed further later, with regard to the cyclic content.

### 2.4.6 Properties of Pyridine Containing Poly(arylene ether)s

The intrinsic viscosities, number average molecular weights, and thermal properties of a series of pyridine containing poly(arylene ether)s are given in Table 2-3. High intrinsic viscosities were reached in times of 20 hours or less for all cases with the exception of the ketimine containing poly(arylene ether). This might possibly have been due to low monomer purity.

By Thermal Gravimetry in air with a heating rate of 10°C per minute, 5% weight loss values occur close to 500°C with the exception of the sulfoxide containing copolymer (5% weight loss value of 408°C) (Figure 2-25). Trace number 3 represents the loss of weight with temperature of the sulfoxide containing copolymer. About a 7 weight % loss occurs at $\approx 400$ °C. This weight loss has been observed in both air and nitrogen in previous studies \textsuperscript{53} and may be caused in part by the chemical transition to the more stable sulfide form. Trace number 4 is for the triphenylphosphine oxide containing copolymer, which shows high char yields at temperatures up to 700°C. This was expected due to the phosphine oxide moieties unique chemistry \textsuperscript{45}. Traces numbers 1 and 2 were more typical of poly(arylene ether)s, and show good dynamic thermal stabilities for pyridine poly(arylene ether)s containing the ketimine and sulfone group. It should be noted that dynamic thermal stabilities alone may not
Table 2-3. Properties of Pyridine Containing Poly(arylene ether)s

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>η¹</th>
<th>&lt;Mₙ&gt; g/mol²</th>
<th>Tg °C³</th>
<th>5 % Wt. Loss⁴</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(EEP-co-EEK)</td>
<td>insol.</td>
<td>insol.</td>
<td>124</td>
<td>500</td>
</tr>
<tr>
<td>P(EEP-co-EEKt)</td>
<td>0.30</td>
<td>17,300</td>
<td>135</td>
<td>485</td>
</tr>
<tr>
<td>P(EEP-co-EESO)</td>
<td>0.78</td>
<td>95,900</td>
<td>138</td>
<td>408</td>
</tr>
<tr>
<td>P(EEP-co-EESO₂)</td>
<td>0.72</td>
<td>31,100</td>
<td>158</td>
<td>500</td>
</tr>
<tr>
<td>P(EEP-co-EPPPO)</td>
<td>0.87</td>
<td>41,900</td>
<td>164</td>
<td>513</td>
</tr>
</tbody>
</table>

1) dL/gram, chloroform, 25°C
2) <Mₙ> measured by GPC in chloroform, relative to polystyrene standards and calculated without low molecular weight peak.
3) Glass Transition Temperature Determined by Differential Scanning Calorimetry at 10°C/min.
4) Air °C
Figure 2-25. Dynamic Thermal Gravimetry in Air (10°C/min) for Pyridine Containing Poly(arylene ether)s at 10°C/minute
sufficient to gauge thermal stabilities, as the behavior observed using dynamic measurements does not necessarily reflect the long term isothermal stability of a given material.

P(EEP-co-EEK) solution crystallized from DMAc (Tm of 250°C observed on first heat by DSC at 10°C/min), but was not observed to crystallize from the melt. This is differed from the 0 - 30 mole % pyridine containing (ether ether ketone)s which all crystallized readily from the melt 2. P(EEP-co-EEK) was insoluble in common solvents at lower temperatures. It was soluble in dipolar aprotic solvents at temperatures of 150°C or higher. None of the other copolymers displayed any crystallinity. In Table 2-4 the glass transition temperatures of the pyridine containing poly(arylene ether)s (following precipitation to remove most of the low molecular weight component) are compared to the analogous series of poly(arylene ether)s where bisphenol A was reacted with the activated dihalides instead of 2,6-bis(4-hydroxyphenyl ether) pyridine. The trend of increasing glass transition temperatures (Tg's) going from ketone to ketimine to sulfoxide to sulphone to phenyl phosphine oxide group is the same, although the Tg's in the pyridine containing poly(arylene ether) series are all about 30°C lower. The decreased Tg's of the pyridine containing poly(arylene ether) series was not surprising, as the 2,6-bis(4-hydroxyphenyl ether) pyridine monomer imparts 4 flexible ether links per one repeat unit, as opposed to only 2 flexible ether links per repeat unit resulting from bisphenol-A.

Size exclusion chromatography experiments revealed significant amounts (≈ 20 wt %) of low molecular weight peaks in all of the pyridine containing poly(arylene ether)s (with the exception of the P(EEP-co-EEK) which
Table 2-4  Comparison of Tg's of Pyridine Ether and Bisphenol A Containing Poly(arylene ether)s

<table>
<thead>
<tr>
<th>copolymer</th>
<th>Tg (°C)</th>
<th>copolymer</th>
<th>Tg (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(EEP-co-EEK)</td>
<td>124</td>
<td>BisA/ketone</td>
<td>150</td>
</tr>
<tr>
<td>P(EEP-co-EEKt)</td>
<td>135</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P(EEP-co-EESO)</td>
<td>138</td>
<td>BisA/sulfoxide</td>
<td>169</td>
</tr>
<tr>
<td>P(EEP-co-EESO2)</td>
<td>158</td>
<td>BisA/sulfone</td>
<td>195</td>
</tr>
<tr>
<td>P(EEP-co-EEPO)</td>
<td>164</td>
<td>BisA/phosphine oxide</td>
<td>205</td>
</tr>
</tbody>
</table>

Tg's of pyridine containing poly(arylene ether)s determined by DSC at 10°C/min.
(After precipitation to remove most of the low molecular weight component.)
was not soluble). The number average molecular weights reported in Table 2-3 were calculated by neglecting this low molecular weight component. Figure 2-26 shows typical chromatograms for the pyridine containing poly(arylene ether)s. The first chromatogram is from the P(EEP-co-EES) poly(arylene ether) following initial precipitation from the DMAC polymerization solvent into water, and shows several low molecular weight peaks at high elution volumes of narrow polydispersity. The second trace is from the same polymer following a second precipitation from chloroform into methanol and shows a substantial reduction in the low molecular weight component. This low molecular weight component was suspected to be cyclic oligomer, as in most condensation polymerizations a small amount of low molecular weight cyclic oligomer occurs. Following the second precipitation, the solvent was collected, and evaporated, leaving a white solid. Analysis by gel permeation chromatography confirmed that these white solids were low molecular weight components. For the P(EEP-co-EEPO) phenyl phosphine oxide containing polymer and the P(EEP-co EESO) containing polymers, these low molecular weight materials were analyzed by direct injection secondary ion mass spectrometry (SIMS). The samples were placed in a viscous liquid substrate (nitrobenzyl alcohol), and directly inserted into the mass spectrometer ionization chamber where the sample vapors were bombarded by a beam of cesium ions. The prevalent parent ion peak resulting from this experiment is the M+1 peak, due to the addition of a proton to the parent compound as a result of the collision of the cesium ion with the nitrobenzyl alcohol. In Table 2-5, the results of this experiment are shown. For both the P(EEP-co-EEPO) and the P(EEP-co EESO), M+1 peaks were observed corresponding to the cyclic oligomers with 1,
Poly(ether ether pyridine co ether ether sulfoxide)

\[ <M_w> \ 350,000 \text{ g/mol} \]
Measured by GPC in chloroform, relative to polystyrene standards

Figure 2-26. Size Exclusion Chromatography Trace of P(EEP-co-EES) with LMW Component
Table 2-5. GC-MS of LMW Component in Pyridine Containing Poly(arylene ether)s

<table>
<thead>
<tr>
<th>Number Ru In Cyclic</th>
<th>P(EEP-co-EEPO) * Mw Theory</th>
<th>M+1 Exp.</th>
<th>P(EEP-co-EESO) * Mw Theory</th>
<th>M+1 Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>569.1</td>
<td>570</td>
<td>493.1</td>
<td>494</td>
</tr>
<tr>
<td>2</td>
<td>1138.2</td>
<td>1139</td>
<td>986.2</td>
<td>987</td>
</tr>
<tr>
<td>3</td>
<td>1707.3</td>
<td>1708</td>
<td>1479.3</td>
<td>1481</td>
</tr>
</tbody>
</table>

*Monoisotopic Mass

(A-B) \( n = 1,2,3 \)

poly(arylene ether) cyclcics with \( n=1 \)
2 and 3 repeat units. The relative amounts of the cyclics were not quantified, as
the ion intensity depends on the sample volatility which varies for the particular
cyclic.

The large amounts of low molecular weight cyclic components are
unusual. The concentration of monomer in the polymerization reaction mixtures
was 12 % w/v monomers to total initial solvent (toluene and DMAc), or 18 % w/v
monomers to DMAc. This polymerization concentration is reasonable, and for
most common poly(arylene ether)s would not normally result in 20 wt. % cyclics.
Several possible explanations come to mind for the high cyclic content
observed. The high cyclic content may reflect the high degree of flexibility
imparted to the pyridine containing poly(arylene ether)s because of the 4 ether
linkages contributed to the poly(arylene ether)s repeat unit structure by the 2,6-
bis(4-hydroxyphenyl ether) pyridine monomer. These flexible ether linkages
enable low energy rotation, and may contribute to the negative free energy of
formation of the cyclics, due to a lack of conformational strain. This possibility
should be studied further using molecular modeling techniques to compare the
pyridine ether containing cyclics to other cyclics formed from bisphenols such
as bisphenol-A, which would not impart as much flexibility to the poly(arylene
ether) mainchain. Another possible explanation lies in the fact that a 1.5 molar
excess of K₂CO₃ was used for relatively long heating times. It has been
previously observed that such an excess of base coupled with long heating
times can allow a rapid degradation of the number average molecular weight. It
would be worthwhile to repeat the poly(aryletherification)s with a smaller excess
of base (1.05 molar) for shorter optimized reaction times, and to note the
influence on cyclic formation.
In poly(arylene ether)s such as the pyridine containing poly(arylene ether)s discussed in this chapter, the initial polymerization reaction results in an alternating repeat unit structure. Ensuing transesterification leading to repeat unit randomization is also possible in these types of polymers, but will only occur when certain conditions are met. Transesterification could occur through two different mechanisms with the same end result.

The first mechanism is through nucleophilic attack by a halide ion. Halide ions are produced as a product of the nucleophilic aromatic substitution reaction, and are then present in the reaction mixture in the form of a sodium or potassium salt, depending upon which base is used. Previous work has suggested that in solvents where the fluoride salt is fairly soluble (for example potassium fluoride in diphenylsulfone at 330°C), sequence randomization via transesterification will occur.

The second method by which sequence randomization can occur is by nucleophilic attack of the phenolate chain end at activated sites along the poly(arylene ether) main chain (Figure 2-27). For the pyridine containing poly(arylene ether)s, in order for randomization through transesterification to occur, the aforementioned nucleophilic attacks by halide ion or phenolate must occur at two different activated carbons, the ether carbon para to the electron withdrawing group, and at the carbon ortho to the nitrogen in the pyridine moiety. Meisenheimer complex formation through nucleophilic attack of halogen ion or chain end phenolate must be energetically favorable at each of these sites for randomization to occur.

$^{13}$C NMR is a useful technique for determining monomer sequence distributions in poly(arylene ether)s $^{49,56}$. The sequence distributions of the
Figure 2-27. Transetherification Mechanism in Pyridine Containing Poly(arylene ether)s
pyridine containing copolymer series were analyzed by $^{13}$C NMR. For example, the $^{13}$C NMR spectrum of P(EEP-co-EESO) is shown in Figure 2-28. For an alternating poly(arylene ether), only one type of triad exists in the polymer chain. Therefore, additional peaks due to differing triad forms will not be present. The small chemical shifts resulting from differing sequences are readily detectable using high field NMR spectrometers. The eleven distinct chemical shifts in Figure 2-28 indicate that the P(EEP-co-EESO) copolymer is in the alternating form and not in the statistically random form. The $^{13}$C NMR spectrum of P(EEP-co-EEK) is shown in Figure 2-29. This ketone containing poly(arylene ether) was analyzed at high temperatures (170°C) in D$_6$ DMSO, as it was not soluble at lower temperatures. 12 distinct peaks were observed, as expected from the 12 carbons in magnetically unique environments in the alternating copolymer. The $^{13}$C NMR spectra for the ketimine, sulfone, and phenylphosphine oxide copolymers also support the proposition that the pyridine containing poly(arylene ether)s are in the alternating form, with the exception of the $^{13}$C NMR spectrum for P(EEP-co-EESO$_2$). This polymer exhibits at least 12 peaks even though there are only 11 carbons in magnetically distinct environments predicted theoretically for the perfectly alternating copolymer. This may be explained by endgroups or cyclic content causing the additional peak. It is suspected that nucleophilic attack to form a stable Meisenheimer complex only occurs at the ether carbon para to the electron withdrawing group, and not at the carbon ortho to the nitrogen in the pyridine moiety. Therefore, it seems reasonable that all of the pyridine containing poly(arylene ether)s synthesized under conditions detailed in this chapter are alternating copolymers.
Figure 2-28. $^{13}$C NMR of P(EEP-co-EESO) Pyridine Containing Poly(arylene ether)
Temperature: 170°C
Sample conc: 6% (w/w)
Solvent: D6 DMSO

Figure 2-29. $^{13}$C NMR of P(EEP-co-EEK) Pyridine Containing Poly(arylene ether)
**Aqueous Dispersibility of Pyridine Containing Poly(arylene ether)s**

Several methods were attempted for forming aqueous dispersions of the pyridine containing poly(arylene ether)s. One method was to precipitate a solution of polymer in THF into acidified water with a pH of 2. Another method was to add HCl in THF to polymer solutions in THF, and to subsequently precipitate the polymer/(THF+HCl) solutions into water. Stable colloidal aqueous dispersions of the pyridine containing poly(arylene ether)s were not achieved using these methods.

**2.5. CONCLUSIONS**

Nucleophilic aromatic substitution has been determined to occur rapidly at the first chlorine on 2,6-dichloropyridine relative to the same reaction at the second chlorine on 2,6-dichloropyridine. To incorporate the pyridine ether moiety into a pyridine containing poly(arylene ether) without utilizing 2,6-dichloropyridine as a monomer, a novel pyridine ether containing monomer (2,6-bis(4-hydroxyphenyl ether) pyridine) has been synthesized, and a purification procedure has been established. Using this new monomer, a series of pyridine containing copolymers with varied chemical composition were synthesized using molecular weight uncontrolled conditions. These pyridine containing copolymers showed good thermal stabilities, and alternating sequence structures. Aqueous dispersions of acidified pyridine containing poly(arylene ether)s were not achieved by the methods used.
2.6. RECOMMENDATIONS FOR FUTURE WORK

To gain further understanding of the poly(aryletherification) and the resulting molecular weight distribution of the pyridine containing poly(arylene ether)s made with the 2,6-bis(4-hydroxyphenyl ether) pyridine, it would be useful to repeat the polymerizations, using a 1.05 molar excess of $\text{K}_2\text{CO}_3$ and optimized reaction times, and a careful study of molecular weight distribution versus time. It would also be informative to utilize molecular modeling to determine if the pyridine ether containing cyclic oligomers have an unusually stable structure that results in high levels during the polymerization.

In light of observations made in the solubility studies of the poly(amic acid) salts in chapter 3, it would be desirable to study a series of protonated or quaternized pyridine containing poly(arylene ether)s where the counterions varied in hydrated diameter, as well as hydrophobicity. It would also be useful to study pyridine containing poly(arylene ether)s where the charge spacing, and the morphologies (ie; semi-crystalline vs. amorphous) were systematically varied. By controlling these variables, a quantitative understanding of the factors involved in attaining water-dispersible/water soluble pyridine containing poly(arylene ether)s could be gained.

2.7. REFERENCES


(2) Brink, A. E.; Lin, M. C.; Riffle, J. S. Chemistry of MATERIALS 1993, 5, 925-929.


(30) Percec, V.; Clough, R. S.; Fanjul, J.; Grigoras, M. Polymer Preprints, ACS Polymer Division 1993, 34, 162-3.

(31) Percec, V.; Clough, R. S.; Rinaldi, P. L.; Litman, V. E. Macromolecules 1994, 27, 1535-1547.


(52) Roovers, J.; Cooney, J. D.; Toporowski, P. M. *Macromolecules* 1990, 23, 1611.


Chapter 3. Preparation of Controlled Molecular Weight Polyimides from Poly(amic acid) Salt Precursors

3.1. SYNOPSIS

In this chapter, the preparation of controlled molecular weight, thermoplastic polyimides via poly(amic acid) salt precursors will be discussed. This research shows the feasibility of processing poly(amic acid) salts from aqueous solutions, then imidizing in the melt to form controlled molecular weight polyimides. This presents an environmentally friendly method for processing polyimides. 2,2'-Bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride and meta-phenylene diamine (the Ultem™ monomers), together with a pre-calculated amount of phthalic anhydride as an endcapping reagent, were reacted in N-methylpyrrolidinone (NMP) as well as in tetrahydrofuran (THF) to form poly(amic acid)s with controlled molecular weights (Figure 3-1).

Figure 3-1. Synthesis of Controlled <M_n> Ultem™ Type Poly(amic acid)
The kinetics of amidization were faster in THF relative to NMP, allowing rapid attainment of pre-calculated, high molecular weights. Synthesis of the poly(amic acid)s in THF also allowed for easier solvent removal through volatilization in contrast to the poly(amic acid) synthesized in NMP (in which case the solvent was removed by precipitation in water, leading to detrimental amide hydrolysis). Poly(amic acid) salts were prepared in heterogeneous reactions of the poly(amic acid)s with quaternary ammonium bases or triethylamine dissolved in methanol or water, to yield soluble salts. The solvents were removed by evaporation and the poly(amic acid) salts were then melt imidized in air at temperatures of 250°C or 300°C for 30 min. The resultant polyimides were characterized by differential scanning calorimetry to determine their glass transition temperatures, universal calibration size exclusion chromatography to determine their molecular weights and distributions (MWD), and by potentiometric titration of any residual aromatic amine content to evaluate any amide hydrolysis which might have occurred during processing. Results suggest that the poly(amic acid) salt counterion controls the mechanism by which the salt imidizes, which in turn controls the properties of the final polyimide. The triethylammonium poly(amic acid) salts yield linear, thermoplastic, polyimides with controlled molecular weights upon melt imidization. The polyimides produced from the poly(amic acid) salts containing the triethylammonium, tetraethylammonium, and tetrapropylammonium counterions showed dynamic weight loss profiles comparable to the polyimide produced directly from the control poly(amic acid).
3.2. INTRODUCTION

Many excellent reviews have been written in the area of condensation polyimide synthesis, properties, and imidization characteristics 1-7. This introduction will focus primarily on areas of polyimide science closely related to this research project.

3.2.1 Condensation Polyimides

Thermoplastic polyimides are typically synthesized via condensation mechanisms, where low molecular weight by-products are produced during the synthesis. Polyimides contain the imide moiety, which is structurally composed of two carbonyls with a nitrogen bonded in between (Figure 3-2). If the R groups bonded to the imide moiety are aromatic in nature, the imide moiety attains excellent thermal stability by virtue of the delocalization of π orbital electrons throughout the imide moiety and adjacent phenyl rings. The partial ladder structure of polymers with these groups probably also contributes to weight retention of these materials at high temperatures.

\[
\begin{align*}
R_1 & \quad \text{C} \quad N \quad R_3 \\
R_2 & \quad \text{C} \quad \text{O}
\end{align*}
\]

Figure 3-2. Imide Chemical Structure
The first polyimide was reported in 1908, when Bogert and Renshaw disclosed that 4-aminophthalic anhydride evolved water upon heating with the possible production of a "polymolecular imide" (Figure 3-3) \(^8\).

\[
\begin{align*}
\text{O} & \quad \text{C} \\
\text{H}_2\text{N} & \quad \text{O} \quad \text{C} \\
\text{C} & \quad \text{O}
\end{align*}
\quad \xrightarrow{\text{heat}}
\quad \begin{align*}
\text{O} & \quad \text{C} \\
\text{C} & \quad \text{N} \quad \text{O} \\
\quad & \quad \text{n}
\end{align*}
\]

4-aminophthalic anhydride

Figure 3-3. Polymerization of 4-Aminophthalic Anhydride

Classically, polyimides are synthesized in a two-step method, where a tetracarboxylic acid dianhydride is added to a solution of diamine in a polar aprotic solvent such as N-methylpyrrolidone (NMP), N,N-dimethylformamide (DMF), or N,N-dimethylacetamide (DMAc), at temperatures between 15 to 75°C \(^9\text{-14}\). A poly(amic acid) is generated which may be later cyclized and dehydrated to a polyimide (Figure 3-4). In the first step, the poly(amic acid) is generated by the nucleophilic acyl attack of the aromatic amine at the anhydride carbonyl. Nucleophilic acyl substitution is a reaction that occurs when a nucleophile such as an alcohol or an amine forms a bond to a carbonyl carbon by nucleophilic addition. The factors facilitating this attack are steric openness at the carbonyl carbon, and the ability of the carbonyl oxygen to accept the electron pair from the carbonyl oxygen bond \(^15\). These reactions are reversible, less so if a highly reactive acyl compound such as an acid chloride is used as a
starting material. The rates of these reactions can be increased by use of an
acid catalyst that coordinates with the carbonyl oxygen, further increasing the
electropositive nature of the carbonyl carbon. In the case that a low molecular
weight product of the reaction can be removed by distillation, this will drive the
reaction to completion. A dipolar aprotic solvent can be useful for these
reactions, in order to solvate charged transition species, and also in the case of
a polyamic acid, to associate with the carboxylic acid proton so as to reduce it's
catalytic activity in the hydrolysis of the amide linkage or the formation of
amine/anhydride from the amide linkage.

The mechanism for the formation of poly(amic acid) is shown in Figure 3-5
\textsuperscript{16,17}. It is important to note the equilibrium arrows in the mechanism. This
\textsuperscript{16,17} denotes that the acid (by the acidic carboxylic proton ) catalyzed reverse
reaction to form anhydride and amine occurs to a significant extent once amic
acid product has formed. It should be noted that if any water evolves during this
process due to imidization, then any anhydride present is susceptible to
hydrolysis. Acting as an inherent aid towards driving this equilibrium toward
high molecular weight poly(amic acid) product, the polar aprotic solvents form
complexes with the carboxylic acid groups of the poly(amic acid), helping to
drive the polymerization to completion by, in effect, removing a product of the
amidization reaction (the carboxylic acid group) by chemical means \textsuperscript{16,17}. The
reactivity of the dianhydride monomer can be uniformly related to its electron
affinity (E\textsubscript{a}), which can be calculated from reduction data obtained in
polarography experiments \textsuperscript{18}. Strong electron withdrawing groups in an
anhydride activate the anhydride for nucleophilic acyl attack on the anhydride
carbonyl. The diamine’s reactivity correlates well to it’s basicity \textsuperscript{19,20}. The rate
Figure 3-4. Two-step synthesis of Polyimide
constants for amidization increase as pKa increases (for the protonated amine), or as basicity increases. Very basic diamines such as aliphatic diamines are not ideal reactants in their underivatized state, as the diamines may form salts with the carboxylic acid product of the amidization, thus upsetting the stoichiometry of reactants, and preventing the attainment of high or controlled molecular weights.

\[ 
\begin{align*}
\text{Figure 3-5. Mechanism for Amine Reacting with Anhydride to form Amic Acid}
\end{align*}
\]

### 3.2.2 Molecular Weight Control in Synthesis of Poly(amic acid)s

Polyimides are often prepared from aromatic dianhydrides and aromatic diamines. One common synthetic approach involves relatively low temperature formation of the poly(amic acid), followed by imidization in the melt at higher temperatures. Carothers originally developed the basic theory for prediction of
polymer molecular mass produced by step polymerization\(^{21}\). He recognized that the number average degree of polymerization (\(<X_n>\)) can be related to the extent of reaction \(\rho\) at time \(t\) by the following relationship:

\[
X_n = \frac{1}{1 - \rho}
\]

where \(\rho = \frac{\text{Number of functional groups reacted}}{\text{Number of functional groups initially}}\)

and \(X_n\) is the degree of polymerization of the reaction mixture (each repeat unit, for a polymer made up of A-A and B-B monomers has \(X_n = 2\)). Therefore, in a step-growth polymerization, if A-A and B-B monomers are used in a perfect 1:1 ratio, (and assuming a high purity system), the resultant molecular weight of the product polymer will be theoretically infinitely high at an extent of reaction of exactly 1. However, it is undesirable to commercially process polymers with infinitely high molecular weights. Above the critical molecular weight for chain entanglement, the melt viscosity of polymer materials is proportional to the weight average molecular weight raised to the 3.4 power. Controlling molecular weight by controlling the extent of reaction \(\rho\) is an unacceptable method, as extent of reaction is difficult to control, and upon processing in the melt, further reaction may take place. If the reaction ratio of A-A to B-B monomers are offset, the average molecular weights (\(<M_n>, <M_w>, <M_z>\)) can be controlled by the extent of the offset, with the average molecular weights decreasing as the offset increases. This decrease in average molecular weights (or in number average degree of polymerization) with increasing
stoichiometric offset is described by the general case of the Carothers equation

\[ \bar{X}_n = \frac{1 + r}{1 + r - 2rp} \]

Where \( r \) is equal to the stoichiometric offset, or \( r = \frac{NA}{NB} \), and is defined so that it is always less than or equal to one.

The \( r \) ratio (and thus the number average molecular weight) may also be controlled by the addition of a monofunctional reagent. This method is particularly desirable, as it enables the synthesis of polymers with non-reactive end-groups, producing polymers with consistent processability, and better thermal stability. The following section will detail the calculation of the amounts of reagents in the case where molecular weight is to be controlled by the addition of a monofunctional reagent in the case of an A-A, B-B step-growth polymerization:

1) First Calculate \( \bar{X}_n \):

\( \bar{X}_n \) for the polymer of interest is calculated by dividing the target Number Average Molecular Weight by 1/2 the molecular weight of the repeat unit:

\[ \bar{X}_n = 2 \frac{Md}{Mru} \]

(where \( Md \) is the target \(<Mn>\) of the polymer, and \( Mru \) is the molecular weight of the repeat unit)

2) Second, Calculate \( r \):

Assuming the polymerization reaction is 100% complete, the stoichiometric imbalance \( r \) is calculated by
\[ r = \frac{\bar{X}_n - 1}{\bar{X}_n + 1} \]

3) **Third, Set up Two Equations with Two Unknowns:**

The stoichiometric imbalance \( r \) is related to the molar amounts of monomers used. Since \( Na \) equals moles of A functionality from A-A monomer and \( Nb \) equals moles B functionality from the B-B monomer, the stoichiometric imbalance may be written as

\[
\text{Equation 1)} \quad r = \frac{Na}{Nb + 2Nb'}
\]

where \( Nb' \) equals the moles of monofunctional reagent added to control the molecular weight. The factor of "2" is present in the equation, because one monofunctional molecule has the same effect in limiting \( \bar{X}_n \) as two molecules of difunctional monomer. The second requirement, as stated above, is that the total moles of "A" be equal to the total moles of "B", or

\[
\text{Equation 2)} \quad Nb + Nb' = Na
\]

An arbitrary value is picked for one of the molar quantities, i.e.; \( Na = 0.1 \). Now equations (1) and (2) may be solved simultaneously to determine values for \( Nb \) and \( Nb' \). The molar amounts calculated may be scaled by multiplication by a constant, to increase or decrease amounts.
Example: Polymerization of an Ultem™ type Poly(etherimide) Polyamic Acid Precursor

\[
\begin{align*}
\text{Bisphenol A Dianhydride} & \quad 520.495 \text{ g/mole (B-B)} \\
\text{Phthalic Anhydride} & \quad 148.118 \text{ g/mole (B)} \\
\text{metaphenylene diamine} & \quad 108.143 \text{ g/mole (A-A)}
\end{align*}
\]

**Target** \( <M_n> = 20,000 \text{ g/mole} = M_d \)

\[
M_{ru} = 520.495 + 108.143 = 628.638 \text{ g/mole}
\]

\[
X_n = \frac{2 \times 20,000 \text{ g/mole}}{628.638 \text{ g/mole}} = 63.63
\]

\[
r = \frac{63.61 - 1}{63.63 + 1} = 0.96905
\]

Let \( N_a = 0.1 \)

\[
a) \quad Nb + 2Nb' = \frac{0.1}{0.96905}
\]

103
(b) \( \text{Nb} + \text{Nb'} = \text{Na} = 0.1 \)

Subtract (b) from (a) and solve for Nb'. Substitute Nb' back into (b) and solve for Nb.

**Results:**

Table 3-1. Results of Calculation of Stoichiometry for 20,000 g/mole PAA.

<table>
<thead>
<tr>
<th>Monomer</th>
<th>moles</th>
<th>g/mole</th>
<th>grams</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dianhydride (B-B)</td>
<td>Nb = 0.09681</td>
<td>.048405</td>
<td>520.495</td>
</tr>
<tr>
<td>Diamine (A-A)</td>
<td>Na = 0.10000</td>
<td>.050000</td>
<td>108.143</td>
</tr>
<tr>
<td>Phthalic Anhydride</td>
<td>Nb' = 3.193E-3</td>
<td>3.193E-3</td>
<td>148.118</td>
</tr>
</tbody>
</table>

**3.2.2.1 Molecular Weight Distribution As a Function of Time in Poly(amic Acid) Synthesis**

For step growth polymerizations the most probable molecular weight distribution \( <M_w>/M_n = 2.0 \) is expected when the reaction has reached its thermodynamic equilibrium state at 100% conversion \( (p=1.000) \). The breadth of the distribution of molecular weights in equilibrium step-growth polymerization may be expressed by

\[
\frac{M_w}{M_n} = 1 + p
\]

However, in the case of a very reactive system, the polymerization mixture will not always be in an equilibrium state, allowing for a deviation from the equation.
The reaction of an aromatic dianhydride with an aromatic diamine to form a polyamic acid is such a reactive system. Typically, when adding a solid aromatic dianhydride in powder form to an aromatic diamine in a polar aprotic solvent like NMP or DMAc an interfacial type polymerization can occur at the dianhydride particle surface (Figure 3-6), and some polymer chains grow quickly to high molecular weight\textsuperscript{22}. This occurs especially when the rate of poly(amicidization) is much greater than the rate of dissolution of the solid dianhydride particle into the polar aprotic solvent. Initially, $<\text{Mw}>/<\text{Mn}>$ may be significantly greater than the most probable distribution of 2.0. However, once the poly(amic acid) is formed, the amide linkages can reversibly cleave, reforming anhydride and amine. Amide interchange can also result a dynamically changing molecular weight distribution. Given sufficient time, due to the equilibrium nature of the formation of poly(amic acid), the most probable distribution of 2.0 will be eventually reached.

The reaction of anhydride with amine is exothermic, and the equilibrium is thus shifted towards polymer (amide) at lower temperatures. If the reaction is run at room temperature, the exotherm of the reaction will drive the reaction temperature to higher temperatures which can result in a faster initial rate of reaction forming the amide linkage, but will shift the equilibrium to the left (reactants) and relatively greater amounts of amine and anhydride will form subsequent to the initial rapid increase in molecular weight, decreasing the initially high $<\text{Mw}>$. The $<\text{Mn}>$ will not change significantly during this equilibration. Thus, after the initial reaction of the anhydride with the amine,
Figure 3-6. Interfacial Type Polymerization in Diffusion Range of Dianhydride Particle.
\(<M_\text{w}/M_\text{n}\) can differ from the most probable distribution 2.0, and the most probable distribution of 2.0 will be reached later, after equilibration is complete.

3.2.3 Imidization of Poly(amic acid)s

3.2.3.1 Thermal

The second step of the polyimide synthesis, the cyclodehydration or imidization step, is as important as the poly(amidization) in controlling the resultant polyimide's final chemical and mechanical properties. When heating a poly(amic acid) thermally to imidization temperatures, the rate of the back reaction to anhydride and amine increases, resulting in a reduction in molecular weight, and the formation of anhydride endgroups visible by spectroscopy at intermediate temperatures (Figure 3-7)\(^{24}\). Since water, which is a product of the imidization, can react with the anhydride groups, dicarboxylic acid groups are also formed (Figure 3-8). Upon further heating, the dicarboxylic acid groups can again cyclize to form an anhydride, which can re-react with an amine endgroup to form an amic acid, which can then imidize. In other words, though the \(<M_\text{n}>\) may decline during thermal imidization, with further heating under the right conditions the \(<M_\text{n}>\) can be recovered. On the other hand, if the kinetics of imidization are so rapid that negligible back reaction to anhydride and amine occurs, a decline in \(<M_\text{n}>\) may never occur.

Under thermal imidization conditions, the isomide polyimide isomer may form. The isomide is thermodynamically less stable than the imide and given sufficient energy for activation by heating, conversion to the thermodynamically stable imide state can occur (Figure 3-9)\(^{25}\).
Figure 3-7. Anhydride Peak Height as Function of Temperature During Poly(amic acid) Imidization\textsuperscript{24}. 
Figure 3-8. Reactions Occurring During Imidization of Poly(amic acid)
Figure 3-9. Thermal Conversion of Isoimide to Imide
3.2.3.2 Melt or Solid State Imidization

Poly(amic acid)s are often cast into a film (or a prepreg) from a polar aprotic solvent, and then imidized. Usually after the film is formed by evaporating the solvent, there is a small amount of dipolar aprotic solvent (such as DMAc or NMP) remaining due to the strong complexation of these solvents to the poly(amic acid). The poly(amic acid) is often imidized in steps, for example 30 minutes at 100°C, 30 minutes at 200°C, followed by 30 minutes at 300°C. At the higher temperatures, the high boiling polar aprotic solvents will completely volatilize and evolve. Such conditions are established empirically, according to the optimal mechanical and/or adhesive properties of the resultant polyimide. The kinetics of thermal imidization under isothermal conditions are greatly dependent upon the temperature of imidization, and the glass transition temperature of the fully cyclized imide. When the imidization temperature is close to or below the glass transition temperature, the imidization reactions have been found to have two major steps. The first step is faster, with a constant rate. The second slower step reflects the decreasing chain mobility during imidization as the glass transition temperature of the polymer increases with degree of imidization. The rate constant for the second step is decreased dramatically and also becomes dependent on conversion.

3.2.3.3 Microwaves as an Energy Source for Fomation of Polyimides

Another method of supplying the energy need for the imidization reaction is via microwave radiation. A recent study by Lewis et al.\textsuperscript{26} has shown that for the case of solution imidizations in NMP using an azeotroping agent, the kinetics of imidization were enhanced by 20 to 34 times that of the analogous
system at the same temperature without microwave radiation. This enhancement was explained by a proposed theory which predicts a locally increased temperature in the vicinity of dipoles, which effectively reduces the activation energy of imidization. 

3.2.3.4 Solution Imidization

The poly(amic acid)s may also be imidized in solution, utilizing a polar aprotic solvent such as NMP and an azeotroping agent such as o-dichlorobenzene to remove the product of the reaction (water) using conditions and techniques established at Virginia Tech. In a detailed kinetic analysis of the solution imidization of four structurally different poly(amic acid)s second-order kinetics were observed at imidization temperatures between 140° and 180°C. The second order kinetic relationship was attributed to an imidization mechanism catalyzed by the carboxylic acid groups on adjacent or nearby repeat units. Molecular weight analysis during imidization revealed an initial rapid drop in molecular weight with time (determined by intrinsic viscosity measurements), followed by increasing molecular weight as the imidization proceeded. The initial drop in molecular weight is likely due to the shift in equilibrium toward anhydride and amine, or to hydrolysis of the amide groups.

3.2.3.5 Chemical Imidization

Poly(amic acid)s may also be imidized chemically as was disclosed by Endrey in 1965. This is accomplished with the use of an anhydride dehydrating agent in combination with a basic catalyst. For example the
combination of acetic anhydride with triethylamine may be used. When weaker bases such as pyridine are used in combination with acetic anhydride, significantly more isoimide linkages were also produced \(^{32}\).

3.2.4 Polyamic Acid Derivatives

3.2.4.1 Poly(amic ester)s

Another poly(amic acid) derivative is the poly(amic ester). Poly(amic ester)s are known to be more hydrolytically stable than the corresponding poly(amic acid), resulting in more uniform films, as the hydrolysis is suppressed in the ester derivatives. They have the added advantage that they do not exhibit the polyelectrolyte effects observed in poly(amic acid)s so they are more amenable to molecular weight characterization by size exclusion chromatography. A particular advantage for microelectronic application results from the fact that water is not released when cured. Generally, poly(amic ester)s imidize at slightly higher temperatures, and with a broader imidization window as compared to the corresponding poly(amic acid)s. This may be partly due to a higher energy of activation for the imidization reaction, and it may also be partially due to the fact that higher temperatures are required to attain a corresponding degree of molecular mobility in a poly(amic ester) as compared to the poly(amic acid) analog.

One method of preparing poly(amic ester)s is by reaction of poly(amic acid) salts with alkyl halides. In one study, alkyl halides highly activated towards nucleophilic substitution, (such as allyl bromide and benzyl bromide), gave the best results with triethylamine poly(amic acid) salts in completely aprotic media \(^{33}\).
In a study by scientists at AT&T Bell Laboratories it was determined a reactivity difference existed between t-butyl poly(amic ester)s and n-alkyl poly(amic ester)s \(^{34}\). This difference was explained by different pathways for respective curing reactions. While the n-alkyl esters imidized through elimination of the n-alcohol, the t-butyl ester imidized by elimination of isobutene followed by rapid imidization of the free carboxylic acid resulting in a faster overall cure rate for the t-butyl ester\(^{34}\). In a more recent study by the same group in search of other rapidly curing poly(amic ester)s, tert-amyl esters of pyromellitic dianhydride were prepared by reaction of the dianhydride with tert-amyl alcohol (2-methyl-2-butanol) \(^{35}\). The tert-amyl poly(amic acid) esters were prepared by a condensation reaction between oxydianiline and the pyromellitic dianhydride ester in the presence of a peptide coupling agent and triethylamine. Analysis of the effluents released during curing by a mass spectrometer coupled with a pyrolyzing probe revealed that imidization occurred completely by elimination of 2-methyl-1-butene \(^{35}\).

Poly(amic ester)s have also been prepared by first forming a dialkyl dihydrogen pyromellitate by reaction of pyromellitic dianhydride with the desired alcohol, and by then converting the dialkyl dihydrogen pyromellitate to the corresponding diacyl chloride by reaction with oxalyl chloride. This activated diacyl chloride monomer is next reacted directly with a diamine such as oxydianiline without additional catalyst or coupling agent to form the poly(amic acid) ester\(^{36,37}\).
3.2.4.2 Ester-Acid Route to Synthesizing Polyimides

The ester-acid route to making polyimides involves a dianhydride monomer that has been subjected to alcoholysis to yield an ester-acid monomer. This monomer is less moisture sensitive than the anhydride, and will generate the dianhydride in situ (generating alcohol) when using NMP with a dichlorobenzene azeotroping agent at temperatures of 170-185°C. An additional benefit of this ester-acid route is that the monomer may be less hazardous to health than either the tetracarboxylic acid or the dianhydride. Once the dianhydride has formed in the reaction mixture, polyamic acid formation and subsequent cyclization will proceed as in Figure 3-4. Because the dianhydride must form in situ prior to the polymerization reaction, the overall rate of this reaction will be much lower than the rate of the direct addition of dianhydride to diamine. The formation of anhydride will be the rate limiting step in the formation of poly(amic acid).

3.2.4.3 Poly(amic acid) Salts

Thermoplastic polyimides such as General Electric's Ultem™ (Figure 3-10) have an excellent combination of thermal stabilities, mechanical properties and processability. Ultem can be processed into desired forms from the melt, or from an organic solvent such as chloroform or DMAc. Higher performance polyimides, with less mainchain flexibility and higher Tg's, often cannot be processed from the melt or from a solvent. These intractable materials must be processed via their soluble poly(amic acid) or poly(amic acid) derivative precursors. The hydrolytic instability of the poly(amic acid) precursors may sometimes preclude easy handling and long term storage.
required in industrial operations. Formation of a poly(amic acid) salt precursor may allow polyimides to be processed from a water soluble precursor, with the possibility of good stability during storage. This processing route could prove valuable for an industry pressed with the necessity to minimize exposure to workers by organic solvents.

Typically polyimides are formed either in organic solvents or from the melt, from poly(amic acid) precursors. Processing from aqueous solution is not possible for water-insoluble polyimides, but presents an environmentally friendly method for processing polyimides via water soluble poly(amic acid) salt precursors. The general method is as follows: first poly(amic acid) is synthesized from dianhydride and diamine monomers, next the poly(amic acid) salt is formed by reaction of the poly(amic acid) with a stoichiometric amount of base, and finally the poly(amic acid) salt is thermally imidized (Figure 3-11). Several examples exist in the literature which utilize this general methodology.

In 1966, Endrey of du Pont de Nemours and Co. disclosed a novel method for the preparation of polyimides, by adding triethylamine to the polymerization solution of the poly(amic acid) in DMF or DMAc, converting either 50 or 100 mole percent of the acid groups to the triethylammonium salts. The poly(amic acid) salt solutions were then imidized chemically or
Figure 3-11. Ultem™ Type Poly(amic acid) to Poly(amic acid) Salt to Polyimide
thermally, yielding polyimides with good mechanical properties. In Endrey's patent, isolation or water solubility of the poly(amic acid) salts was not disclosed. In a study reported by Kreuz and coworkers (also of du Pont de Nemours and Co.), tertiary amine salts were formed (utilizing 1:1 stoichiometry) following formation of the poly(amic acid) of pyromellitic dianhydride (PMDA) and 4,4'-diaminodiphenyl ether in DMAc. The kinetics of imidization were treated as having an initial fast first order step, followed by a subsequent slower first order step at higher conversions. An important result of this study was the discovery that the initial rate of cyclization (at 161°C) was between 4 to 10 times faster for the tertiary ammonium salts as compared to the poly(amic acid) alone. The rates calculated for the slower second step were also seen to increase slightly, though not as much as for the first step. In a study by Seddon and Reynolds, it was reported that powdered poly(amic acid) prepared from PMDA and 4,4'-diaminodiphenyl ether was dissolved in aqueous solutions of 90 to 150 mole % of triethylamine to form a 2% w/v solution. The viscosities of the poly(amic acid) salt solutions were monitored with time, and the solutions with greater than 100% base relative to -COOH showed excellent retention of initial viscosities. A U.S. patent (1975) disclosed a method of preparing water soluble poly(amic acid) salts utilizing an α, ω-aminopoly(amide) with an equivalent weight of 1000 or less as the diamine, and subsequent addition of NH₃ or aliphatic amines. These materials are obviously not of highest thermal stability and mechanical integrity due to the flexible poly(amide) spacer, but they could potentially perform well as varnishes or binding agents which could be processed from alcohol or water. In another example of a water soluble polyimide composition, 1,2,3,4-butane tetracarboxylic acid is reacted
Figure 3-12. Influence of Mole % Base to -COOH on Stability of Aqueous Triethylammonium Poly(amic acid) Salt Solutions (2.0% w/v)\textsuperscript{42}. 

119
with a diamine such as 4,4'—diaminodiphenylmethane to form a poly(amic acid), which was imidized at 100-130°C until a residual acid value of 20-35% was achieved. At this point the reaction was allowed to cool to 80 - 100 °C, and an aqueous ammonia solution was added to form an ammonium salt of the poly(amic acid). It is likely that such rigorous conditions would result in significant hydrolysis of amide groups, resulting in decreased molecular weight.

Water solubility is enhanced by neutralizing the poly(amic acid)'s carboxylic acid groups with an excess of a suitable base. In the research discussed in this chapter we were particularly interested in exploring these aspects for composite applications. Aqueous solutions of poly(amic acid) salts may make excellent fiber sizing media. The salts could subsequently be imidized to yield thermoplastic, relatively water insensitive, fiber-matrix interphase layers. Aqueous based polyimide precursors might also be appropriate as components of waterborne polymeric resins as curing or toughening reagents for thermoset matrices.

There may also be technical advantages other than water solubility in preparing polyimides from the salt form as opposed to the more conventional direct process via the poly(amic acid). The hydrolytic stability of poly(amic acid) salts may be increased relative to the poly(amic acid) since the acid catalyzed back reaction to amine and hydrolytically unstable anhydride is suppressed. Another possible advantage in forming polyimides from poly(amic acid) salts is found in enhanced imidization rates of tertiary ammonium poly(amic acid) salts relative to the imidization rates of free carboxylic acids. Kreuz and coworkers found that tertiary ammonium salts of poly(amic acid)s had initial cyclization rates 4 to 10 times that of the free poly(amic acid). This should limit
depolymerization during the imidization which can result in reduced polyimide molecular weight, especially in the presence of water 30,44,45.

The focus of this study is on the effects of different cations on (1), water solubility and (2), on the properties of the polyimides imidized in the melt state from the salt precursors. Control of polyimide molecular weight under these conditions, together with avoiding crosslinking reactions, will be key issues since mechanical properties are known to be a function of both factors. Some emphasis will also be placed on reaction conditions for forming poly(amic acid)s since rapid attainment of desired molecular weights is of practical importance.

Poly(amic acid) salts have been made and imidized previously, but absolute molecular weight analyses of the precursor poly(amic acid)s and resultant polyimides were not conducted 41,42. In some cases, the conditions used to prepare the poly(amic acid) salts are suspected to result in hydrolysis of the poly(amic acid)40,46. Studies have shown that controlled molecular weight polyimides may be realized from poly(amic acid)s,47,48 but controlled molecular weight polyimides have not been reported via imidization of poly(amic acid) salt precursors. The molecular weight distribution of a thermoplastic engineering polymer is critical to achieving the desired mechanical properties and processability.

During the synthesis of a poly(amic acid) from dianhydride and diamine monomers the rate of polyamidization can be influenced by the solvent chosen for the synthesis. Ether solvents such as THF can be used to produce high molecular weight poly(amic acid)49. Importantly, less basic solvents such as THF, may not form complexes as tightly with an amic acid, effectively freeing the
carboxylic acid proton of the amic acid to catalyze both the forward and reverse reaction. Such autocatalytic reversible kinetics have been observed in THF by Kaas\textsuperscript{50} In the same study by Kaas, it was observed that lower reaction temperatures for synthesis of the poly(amic acid) in THF (10\textdegree{}C to -10\textdegree{}C) resulted in higher molecular weight polyimide (following chemical cyclization of the poly(amic acid)) \textsuperscript{50}. Also, lower critical solution temperature behavior has been observed for some poly(amic acid)/ether solutions resulting in precipitation during polymerization, when the polymerization temperature was too high \textsuperscript{51}.

The present work has been an effort to study the feasibility and issues related to synthesis of controlled molecular weight distribution polyimides via water soluble poly(amic acid) salt precursors.

\subsection*{3.2.5 Molecular Weight Characterization of Poly(amic acid)s and Polyimides by Size Exclusion Chromatography}

Size Exclusion Chromatography (SEC) is an excellent method for establishing the success of preparing controlled $\langle$Mn$\rangle$ poly(amic acids) (PAA) especially given recent advances in the analysis of poly(amic acid)s and polyimides \textsuperscript{48,52-54}. It is important when establishing a polymerization's success to characterize the molecular weight distribution (MWD) of the product polymer. A method such as solution light scattering alone would not establish the MWD of the PAA sample. Size exclusion chromatography, as well as giving absolute values for Mn, Mw, and Mz when used in the Universal Calibration mode, also gives a complete picture of the molecular weight distribution of the product.
polymer. The theory behind Universal Calibration SEC is that two different polymers which elute at the same time from an SEC column will have identical hydrodynamic volumes, and since $[\eta]_\text{M}$ is a direct function of the hydrodynamic volume in very dilute solutions, the relationship between two polymers $[\eta]_1 M_1 = [\eta]_2 M_2$ will hold true. This technique requires that the size exclusion chromatograph be equipped with a differential viscosity detector. Analysis of the PAA directly suffers from the polyelectrolytic nature of the partially ionized carboxylic acid groups on the PAA which can lead to exclusion effects where the polymer chain is extended to the point where it can no longer pass through the gel pores, or to absorption effects, where the PAA absorbs onto the column packing or walls. Either effect will render molecular weight analysis impossible\textsuperscript{53}.

For convenience, it was desirable to utilize the same solvent system for both the poly(amic acid) and polyimide molecular weight analysis by SEC. Cotts and co-workers successfully used NMP stirred over $\text{P}_2\text{O}_5$ for separation of PAA\textsuperscript{52,55}. A study by Konás et al. investigated SEC of soluble, solution cyclized polyimides and their polyamic acid precursors\textsuperscript{53}. An oxydiphthalic anhydride/oxydianiline (ODPA/ODA) poly(amic acid) was analyzed, and it was observed that chain conformation expansion due to a polyelectrolyte-like effect resulted in shifting and splitting of the SEC peaks in pure NMP. These effects were suppressed by stirring the NMP over $\text{P}_2\text{O}_5$ prior to its use as an SEC eluent. Addition of LiBr resulted in adsorption of the PAA onto the polystyrene gel, rendering this solvent system useless for the SEC of PAA's (Figure 3-13). A polyelectrolyte like effect resulted when the ODPA/ODA polyimide was
Figure 3-13. Viscosity chromatogram of (a) ODPA/ODA polyamic acid and (b) oxydiphthalic anhydride/diaminodiphenylsulfone (ODPA/DDS) polyimide in 1. distilled NMP, 2. NMP stirred over \( \text{P}_2\text{O}_5 \), 3. NMP with 0.06 M LiBr \(^{53} \).
analyzed using the distilled NMP, but no such effect was observed in either NMP/P$_2$O$_5$ or NMP/LiBr for the polyimide (Figure 3-13).

Normal retention behavior occurred for the polyimides in CHCl$_3$, THF, and NMP containing LiBr, or in NMP stirred over P$_2$O$_5$. In NMP without any additive, an additional peak at low elution volume, near the exclusion limit of the crosslinked polystyrene column used was typically observed for the polyimides. Only a small quantity of LiBr (0.006M) in NMP was required to suppress this undesirable behavior. The behavior that the polyimides exhibited would be considered typical for ionizable polyelectrolytes such as PAA, but as a fully cyclized polyimide has no ionizable groups, the behavior should not be caused by a polyelectrolyte effect. No increase in solution viscosity was observed for the polyimide in NMP relative to the polyimide in NMP with added LiBr. A speculative explanation proposed for the leading retention behavior for the polyimides in pure NMP is that a form of charge transfer complexation is occurring between the NMP and the cross-linked polystyrene gel which results in exclusion of polyimides, due to the high density of lone pairs present on the imide oxygen and nitrogen atoms.$^{53}$

In a second paper by Konás et al. on SEC characterization of polyimides, it was determined that the Universal SEC calibration using polystyrene standards was valid in all solvent mixtures used (NMP, NMP + 0.6% LiBr, NMP stirred over P$_2$O$_5$, THF, and CHCl$_3$) for the six different soluble polyimides studied.$^{54}$ The number and weight average molecular weights determined in the different solvents showed good agreement, and also agreed with weight average molecular weight values determined by low-angle laser light scattering (LALLS) in NMP.
3.3. EXPERIMENTAL

3.3.1 Materials and Their Purification

2,2'-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride:
Purified, monomer grade, 2,2'-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane
dianhydride (bis A-dianhydride) was kindly donated by the General Electric Co.
It was vacuum dried overnight at approximately 140°C to ensure complete
anhydride cyclization prior to use. (m.p. 189.1-191.1°C)

\[ \begin{align*}
\text{O} & \quad \text{O} \\
\text{O} & \quad \text{CH}_3 \\
\text{O} & \quad \text{O} \\
\text{O} & \quad \text{O}
\end{align*} \]

Tetrahydrofuran (THF): THF, (EM Sciences) was refluxed over sodium metal
with a small amount of benzophenone (which formed the purple sodium
benzophenone ketyl) and was distilled immediately prior to use. (b.p. 67 °C)

\[ \text{O} \]

126
m-Phenylenediamine (mPDA): mPDA - (Aldrich) was sublimed twice under reduced pressure using an 80°C bath and stored under Argon in the dark prior to use. (m.p.64-66 °C)

Phthalic anhydride (PA): PA, (Aldrich 99% ACS Reagent Grade) was also sublimed under reduced pressure using an 80°C bath. (m.p. 131-134 °C)

N-Methyl pyrrolidinone (NMP): NMP, (Fisher Purified Grade) was vacuum distilled after stirring over P₂O₅ in an Argon atmosphere and stored under argon prior to use. (b.p. 205°C/760 mm)

Tetramethylammonium hydroxide (TMAH, 25 wt. % in MeOH) was purchased from Kodak.
Tetraethylammonium hydroxide (TEAH, 25 wt. % in MeOH) was purchased from Acros.

Tetrapropylammonium hydroxide (TPAH, 1.0 M in water) was purchased from Aldrich.

Triethylamine: Reagent grade triethylamine (TEA, neat) was purchased from Fisher.

Tetrabutylammonium hydroxide (TBAH, 25 wt. % in MeOH) was purchased from Fluka.

All bases were titrated with standardized HCl prior to use.
3.3.2 Synthesis of Poly(amic acid) in NMP by a Homogeneous Method

2,2'-Bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride (bis-A dianhydride) (6.4889 g, 0.012467 mole) was weighed into a clean, dry, 250 mL round bottom flask equipped with a magnetic stir bar and sealed with a septum. The flask was twice evacuated and purged with argon. NMP (about 80 mL) was added to this flask by cannula with stirring, and the bis A-dianhydride dissolved. m-Phenylene diamine (1.3913 g, 0.012865 mole) and phthalic anhydride (0.1198 g, 0.0008089 mole) were weighed into a second clean, dry, 100 mL round bottom flask equipped with a magnetic stir bar. Then the flask was sealed with a septum, and purged with argon. By cannula, 25 mL of NMP was added. The m-phenylene diamine and phthalic anhydride dissolved, and were allowed to react for 20 minutes with stirring. Next, the contents of the 100 mL flask were added by cannula to the 250 mL flask with stirring (time = 0 min. in Figure 3-15). The 100 mL flask was rinsed twice with 10 mL of NMP, and this was added to the 250 mL flask by cannula. Aliquots were removed periodically using a clean dry syringe. The samples were 4-5 mL in volume, and were precipitated into 250 mL deionized water stirring rapidly inside a Waring blender. The samples were collected using an aspirated Büchner Funnel. The samples were washed well with deionized water, and were further dried in vacuo at 20°C for 48 h. The exposure time of the poly(amic acid) samples to water was greatest in the case of the first two samples (the 15 minute sample and the 45 minute sample in Figure 3-15) as the fine nature of the precipitates required a greater time for filtration. After the reaction had proceeded for 2 hours the viscosity had increased. The samples were analyzed for solvent content by gravimetric imidization, and were then analyzed using Size
Exclusion Chromatography to determine the absolute molecular weight distributions.

3.3.3 Synthesis of Poly(amic acid) in THF by a Homogeneous Method

2,2'-Bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride (bis-A dianhydride) (58.4002 g, 0.112201 mole) was charged to a clean, dry, 2L round bottom flask equipped with a magnetic stir bar. The flask was sealed with a rubber septum, then evacuated and purged with argon twice. Freshly distilled THF (about 1 L) was added by cannula, and with stirring, the bis A-dianhydride dissolved. m-Phenylenediamine (12.5211 g, 0.115783 mole) and phthalic anhydride (1.0783 g, 0.0072802 mole) were weighed into a clean, dry 250 mL flask equipped with a magnetic stir bar. The flask was sealed with a rubber septum and purged for 5 minutes with argon. About 100 mL of THF was added by cannula, and stirring was commenced for a period of 15 minutes to allow the phthalic anhydride and the m-phenylenediamine time to dissolve and react.

Next the solution in the 250 mL flask was added to the solution in the 2L flask by cannula with stirring (time = 0 minutes in Figure 3-15). The 250 mL flask was rinsed out twice with 15 mL of THF which was added to the 2L flask using a cannula. The solution became viscous almost immediately. Samples of about 2-3 mL were removed periodically from the reactor for SEC analysis using a clean dry syringe and were transferred to small teflon containers. Each sample was immediately placed in a vacuum oven at 20°C to rapidly remove most of the solvent. After 21 hours, the poly(amic acid) solution was poured into a shallow teflon container (11" x 8" x 2") and placed inside a covered glass container equipped with a nitrogen sweep, and was exposed to a brisk nitrogen
flow at room temperature for several days to evaporate most of the solvent. The poly(amic acid) was then dried further for 48 hours under high vacuum at 20°C. A tough clear amber glass resulted, weighing 97.1 grams, corresponding to 25.8 wt. % THF remaining in the material. The samples were analyzed by $^1$H NMR and by gravimetric imidization for solvent content, and were then analyzed using Size Exclusion Chromatography to determine the absolute molecular weight distributions.

### 3.3.4 Determination of Wt. % Solvent in Poly(amic acid)

In order to calculate stoichiometries correctly while preparing the poly(amic acid) salts (PAAS), and also to obtain accurate molecular weight data by SEC using dual viscosity and refractive index detectors, it was important that the wt % solvent remaining in the poly(amic acid) samples be accurately known. Three methods were used to determine this. Residual THF in the poly(amic acid) sample described above is discussed as an example. By comparing the weight of poly(amic acid) obtained as compared to the theoretical yield, a value of 25.8 wt % THF remaining was determined. A second sample was imidized in an air convection oven by heating from 30 to 330°C at 3°C/min, followed by holding the temperature for 30 min at 330°C. Upon cooling and comparing the weight to the initial weight, a value of 26.0 wt. % THF was calculated, assuming quantitative imidization with loss of water, plus solvent loss (gravimetric imidization method). A third method utilized $^1$H NMR on a Varian 400 MHz instrument. The peak area due to the 4 THF protons at 3.6 ppm was compared to the peak area resulting from the 2 amide protons per poly(amic acid) repeat unit at 10.4 ppm to calculate a value of 25.6 wt. % THF in the poly(amic acid)
sample. One or more of these methods were used to determine the wt. % solvent in all poly(amic acid) samples to be analyzed by SEC, so that the actual weight of poly(amic acid) could be used to calculate absolute molecular weight distributions, and so that accurate stoichiometries could be measured when preparing the poly(amic acid) salts. All of the methods were found to be accurate, but the gravimetric imidization method was the most convenient method for most samples.

3.3.5 Preparation of Poly(amic acid) Salts

The poly(amic acid) synthesized in THF was ground to increase the surface area to volume ratio and to further reduce the THF content, by using a 50 gram capacity mill with the aid of liquid nitrogen to decrease the toughness and prevent heating (and the resultant imidization) of the poly(amic acid). Grinding was conducted in a nitrogen atmosphere to prevent moisture condensation on the cold poly(amic acid). Following grinding, the fine poly(amic acid) powder was again dried at 20°C in a vacuum oven for 48 h. After this process, the poly(amic acid) was determined to contain 18.7 wt. % THF by the gravimetric imidization method.

All of the bases used to prepare poly(amic acid) salts were carefully titrated prior to salt preparation with 0.025 N HCl that was previously standardized against Na₂CO₃. The poly(amic acid) salts were prepared as follows: Thirty mL of solvent, methanol or water, was charged into a 100 mL round bottom flask equipped with magnetic stir bar. The volume of base needed to supply a 10 % molar excess relative to the carboxylic acid groups was added (0.004900 mole) using a volumetric pipet. Next 1.400 grams (0.002227 mole repeat units) of powdered poly(amic acid) was added to the
<table>
<thead>
<tr>
<th>Base (solvent for base)</th>
<th>PAAS Solvent (mL)</th>
<th>g PAA</th>
<th>base / COOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetramethylammonium Hydroxide (me)</td>
<td>Methanol (30)</td>
<td>1.4</td>
<td>1.10</td>
</tr>
<tr>
<td>Tetraethylammonium Hydroxide (me)</td>
<td>Water (30)</td>
<td>1.4</td>
<td>1.10</td>
</tr>
<tr>
<td>Tetraethylammonium Hydroxide (me)</td>
<td>Methanol (30)</td>
<td>1.4</td>
<td>1.10</td>
</tr>
<tr>
<td>Tetrapropylammonium Hydroxide (aq)</td>
<td>Water (30)</td>
<td>1.4</td>
<td>1.10</td>
</tr>
<tr>
<td>Tetrabutylammonium Hydroxide (me)</td>
<td>Methanol (30)</td>
<td>1.4</td>
<td>1.10</td>
</tr>
<tr>
<td>Triethylamine (neat)</td>
<td>Methanol (30)</td>
<td>1.4</td>
<td>1.02</td>
</tr>
<tr>
<td>Control (no base)</td>
<td>none</td>
<td>1.4</td>
<td>none</td>
</tr>
</tbody>
</table>
flask, and the flask was sealed with a rubber septum. The mixture was stirred, and as the poly(amic acid) salt formed, a clear, homogeneous solution resulted. The methanolic salts typically formed in 1 hour or less, while the aqueous salts required stirring overnight. The quantities used are summarized in Table 3-2. Once the poly(amic acid) salts had formed homogeneous solutions, the solvents were evaporated under a nitrogen flow, and the poly(amic acid) salts were further dried in vacuo at 20°C for 48 h. The poly(amic acid) salts formed transparent films upon drying. The experimental yields corresponded to the expected theoretical yields plus 0-10 wt % residual solvent. The poly(amic acid) salts were analyzed by thermal gravimetry.

3.3.6 Thermal Imidization of Poly(amic acid) Salts

The poly(amic acid) salts were imidized using a Fisher Scientific Isotemp Programmable Oven Model 838F, with air convection. Two heating programs were used for each material, 250°C for 30 minutes and 300°C for 30 min. Weight losses during imidization were determined and compared to theoretical values. Polyimides resulting from the imidization were analyzed by SEC, potentiometric titration for aromatic amine, and DSC.

3.3.7 Determination of the By-products from Melt Imidization of Poly(amic acid) Salts

Each of five poly(amic acid) salts of the Ultem type poly(amic acid)s were analyzed using gas chromatography-mass spectrometry of the effluents from the imidization: (1) tetramethylammonium poly(amic acid) salt, (2) tetraethylammonium poly(amic acid) salt, (3) tetrapropylammonium poly(amic acid) salt, (4) tetrabutylammonium poly(amic acid) salt, and (5) triethylammonium poly(amic acid) salt. All of the salts analyzed in this manner
had been originally prepared in methanol with the exception of the tetrapropylammonium salt which had been prepared in water. An example of the procedure for these analyses is described below.

A poly(amic acid) salt sample (60-100 mg) was placed in a 10 mL test tube and sealed with a rubber septum. One end of a double ended, 12", 20 gauge cannula was pierced through the rubber septum. The other end of the cannula was directed through a second rubber septum into a second 10 mL test tube (cold trap) placed in a bath of liquid nitrogen (Figure 3-14). A slow helium purge was introduced into the test tube containing the sample which flowed from the sample container, through the cannula, and out through the cold trap via a mineral oil bubbler. It should be noted that helium was chosen as the purge gas as it would not condense in the liquid nitrogen cold trap. Without a gas purge, no condensate was collected. The low liquid nitrogen temperature, -195°C, was deemed necessary to trap the anticipated low boiling by-products.
of the imidization. After cooling the cold trap in the liquid nitrogen bath, the test
tube containing the sample was placed in a 250°C poly(phenylmethylsiloxane)
oil bath for 10 minutes. During the 10 minute heating period, condensates were
observed dripping into the cold trap. The imidization was judged to be
complete in the 10 minute period due to the cessation of condensate formation.
The cannula was removed, then the sample was removed from the cold trap
and warmed to room temperature.

3.3.8 Analysis of Imidization By-products by Gas
Chromatography-Mass Spectrometry

A Fisons GC 8060 coupled with a Fisons VG QUATTRO Mass
Spectrometer was used to analyze the samples. The DB-5MS column, 15m
long, 0.25mm i.d., with a 0.25μm film was purchased from J & W Scientific. The
gas chromatograph column temperature was 35°C. Helium was used as the
mobile phase, at a flow rate of 1 mL/min. The pressure at the column head was
5 psi. For the tetramethylammonium, tetraethylammonium, and
triethylammonium poly(amic acid) salts, all of the collected volatiles vaporized
in the sealed sample container when warmed to room temperature. For the
tetrapropylammonium and tetrabutylammonium poly(amic acid) salts, a
condensed phase was visible at room temperature, which vaporized upon
heating to 80°C. Utilizing a 1 mL syringe, 0.2 mL of the vapor head space of the
samples was injected directly into the gas chromatograph.

3.4. CHARACTERIZATION

3.4.1 Size Exclusion Chromatography

SEC was conducted on a Waters GPC/ALC 150-C chromatograph
equipped with the differential refractometer detector (RI) connected in parallel to
a differential viscometric detector (DV) Viscotek® model 100. The injector and column compartment, connecting line, and DV detector were individually controlled to the same temperature (60 °C). The signals from the RI and DV detectors permitted calculation of intrinsic viscosity and intrinsic viscosity distribution for universal calibration purposes by using Viscotek software Unical 4.04 assuming that the polymer concentration at the outlet of the SEC columns approaches infinite dilution due to separation and column dispersion. The mobile phase was NMP (Sigma-Aldrich HPLC grade) stirred over P₂O₅ (0.02 M) and was prepared according to Cotts et al. ⁵² and Kim et al. ⁵⁵. A flow rate of 1mL/min was used. The columns were Styragegel HT with nominal pore sizes of 10³ and 10⁴ Å. The injection volume was 200 μL with a sample concentration of ≈ 4 mg/mL.

3.4.2 Thermal Gravimetry

Thermal stability of the control poly(amic acid) and the poly(amic acid) salts were determined dynamically in air by measuring weight loss while heating at a rate of 10°C/min. The instrument used was a Dupont Instruments Model 951 Thermogravimetric Analyzer and was calibrated against indium. Small sample sizes of approximately 4 mg were used, as the samples tended to foam upon heating, resulting in mechanical interference during the determination of larger samples.

3.4.3 Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) was performed on a Seiko 220C instrument under nitrogen purge, which was calibrated with indium, tin and zinc. Samples were scanned from 100°C to 250°C then cooled quickly and
scanned a second time from 100°C to 250°C. All scanning rates were 10°C/min. No melting type endotherms were observed. The glass transition temperatures measured from the first scan and the second scan were all within ±1°C.

3.4.4 Potentiometric Titration of Polyimides for Residual Amine

Potentiometric titrations were used to determine the residual aromatic amine content in the imidized poly(amic acid) salt samples. Titrations were performed using a MCI GT-05 (COSA Instruments Corp.) automatic potentiometric titrator. Between 0.25 and 0.3 gram of polyimide was dissolved in 50 mL of chloroform (EM Science HPLC Grade) with stirring. After the samples were completely dissolved, 18-25 mL of glacial acetic acid (Fisher Scientific ACS Plus) was added. Note that smaller amounts of acetic acid were used when this was necessary to avoid phase separation of the solution. The samples were potentiometrically titrated with a solution of HBr in AcOH (0.0137 N) standardized against potassium hydrogen phthalate. The endpoints of the titration were calculated by the auto-titrator as the inflection point in the potential vs. volume titrant plot. Duplicate titrations were performed for each poly(imide) sample and the results were averaged. The moles of imide functionality per mole amine functionality were calculated as shown in the following example.

\[
\frac{\text{mole} \cdot \text{imide}}{\text{mole} \cdot \text{amine}} = \frac{0.2790 \text{g} \cdot \text{imide} \div (1 \text{mole} / 296.31 \text{g})}{0.0137 \text{N} \cdot \text{HBr} \cdot 2.599 \cdot 10^{-3} \text{L}} = 26
\]
3.5. RESULTS AND DISCUSSION

Reactions to form poly(amic acid)s were compared in THF versus NMP at
a concentration of 0.1 mole/L of the dianhydride monomer, and the molecular
weights over time were analyzed. Both reactions were conducted by using
phthalic anhydride as a monofunctional endcapping reagent with targeted
number average molecular weights (<M_n>) of 20,000 g/mole. The Carothers
equation\textsuperscript{21} was employed to determine the amount of phthalic anhydride
needed. Homogeneous reaction conditions were used in order to monitor the
progress of molecular weight growth without any complications from initially
skewed molecular weight distributions which might result from the interfacial
type heterogeneous reactions (when one of the monomers is added to the
reaction mixture in the solid form)\textsuperscript{48,56,57}. The molecular weight distributions of
the poly(amic acid) samples obtained over time were analyzed by universal
calibration SEC techniques developed recently utilizing an NMP mobile phase
which had been stirred over P_2O_5 and polystyrene standards\textsuperscript{48,52-55}. Results
for the synthesis of the poly(amic acid)s in NMP and THF are shown in Figure 3-
15. The data shown in Figure 3-15 demonstrate that the weight average
molecular weight of the poly(amic acid)s prepared in THF reached a high value
quite near the targeted value quickly, in less than 20 minutes, while the
poly(amic acid) synthesized in NMP required about 15 hours to reach a plateau
for the weight average molecular weight. Because both polymerizations were
conducted at the same molar concentrations, this indicates that the rate of
amidization in dry THF was rapid in comparison to the rate of amidization in dry
Figure 3-15. Molecular weights of Ultem poly(amic acid)s monitoring progress of the reactions over time (0.1 M dianhydride concentration).
NMP. The target $<M_N>$ in both reactions was 20,000 g/mole. Figure 3-15 shows the attainment of a number average molecular weight of only 7,000 g/mole. All of the SEC traces of the poly(amic acid) synthesized in both NMP and THF showed a small low molecular weight peak consisting of about 1-5 wt. % of the total sample. In Figure 3-16 the SEC traces for the poly(amic acid) samples taken after short polymerization periods in THF (20 minutes) and in NMP (15 minutes) are shown. A distribution of small low molecular weight peaks are present. These small peaks are suspected to be due to low molecular weight cyclic oligomers formed as a result of the relatively low concentration of monomers used for the polymerizations (6.5 wt/v %). The cyclic formation is not unexpected, in fact the formation of cyclic oligomers during polycondensation reactions is well known. The more dilute the polymerization conditions, the greater the likelihood of intra-molecular reaction to form cyclic versus intermolecular reaction to form linear polymer. The probability of higher molecular weight cyclic formation similarly decreases as the reactive species become separated by greater distances in the reactive linear polymer. In Figure 3-16 it may be seen that the molecular weight of the poly(amic acid) synthesized in NMP (15 minutes) is much less than the molecular weight of the poly(amic acid) synthesized in THF (20 minutes). (Note: This result is not completely representative of the true molecular weights of the poly(amic acid)s in the respective solutions, as the poly(amic acid) synthesized in NMP has it's molecular weight reduced by the procedure of isolation by precipitation in water.) The presence of a small weight percentage of such a species reduces the calculated $<M_N>$ greatly. In the case of the poly(amic acid) samples synthesized in THF, the molecular weight averages were recalculated,
Figure 3-16. Size Exclusion Chromatography Traces of Poly(amic acid) Synthesized in THF and NMP
neglecting the small weight percentage of low molecular weight species (Figure 3-17). The number average molecular weight was calculated to be about 15,000 g/mole by neglecting the low molecular weight peak. For the final poly(amic acid) product, from which the solvent was evaporated more slowly, the molecular weight increased further, reaching a number average molecular weight of about 16,500 g/mole. This may be due to 1) the equilibration of cyclic to linear species forming more linear species with increase in concentration, or 2) a re-equilibration of low molecular weight oligomeric species resulting in an increase in molecular weight.

3.5.1 Theoretical $<M_n>$ vs. Time for Poly(amic acid) Synthesized in NMP and THF.

It is desirable to compare the empirical values of $<M_n>$ versus time for the poly(amic acid)s to the theoretical values. The theoretical curve may be calculated utilizing the 2nd order rate equation combined with the Carothers equation for calculating the average degree of polymerization, $<X_n>$, given a selected reactant ratio $r$, and extent of reaction $p$ at time $t$:

$$X_n = \frac{1+r}{1+r-2rp}$$

where the reactant ratio is defined as

$$r = \frac{N_A}{N_B + 2N_{RB}}$$

where $N_A$ and $N_B$ are respectively the moles of A and B functional groups, and $N_{RB}$ is the moles of monofunctional reagent.
Figure 3-17. SEC results for the $\langle M_n \rangle$ and $\langle M_w \rangle$ molecular weights of Ultem™ type Poly(amic acid)s (0.1 mole/L dianhydride conc.) polymerized in THF not including the low molecular weight peak in the calculations.
By assuming the equal reactivity of functional groups, the kinetic treatment of step polymerization is greatly simplified. For the reaction of a dianhydride with a diamine to form a poly(amic acid), this assumption presumes that the reactivity of a functional group is independent of the molecular weight of the gross molecule to which it is attached. So, for the reaction of a dianhydride with a diamine to produce a poly(amic acid) the rate of reaction may be represented as

\[- \frac{d[A]}{dt} = k[A][B]\]

For the case where the anhydride group concentration is equal to the amine group concentration (and this is the case when controlling molecular weight with a mono-functional reagent), integration of this equation results in

\[\frac{1}{c} - \frac{1}{c_0} = kt\]

which is the familiar integrated form of the 2nd order rate equation. This expression may be rewritten in terms of the extent of reaction \( p \) recognizing that

\[\frac{c_0 - c}{c_0} = p\]

The integrated form of the rate equation may then be rewritten in terms of \( p \)

\[\left( \frac{1}{1-p} \right) = C_0 kt + 1\]
or alternatively

\[ p = \frac{C_o k t}{C_o k t + 1} \]

By substituting \( p \) into the Carothers equation, and multiplying by the mean molar mass of a monomer unit, we can solve for \( \langle M_n \rangle \) as a function of time:

\[ \overline{M}_n = 314 \cdot X_n = 314 \cdot \frac{1+r}{1+r-2rp} \]

Using this equation, an initial functional group concentration of 0.20584 M and the reactant ratio \( (r) \) value of 0.96906 which gives a number average molecular weight value of 20,000 g/mole for the Ultem™ type poly(amic acid) with complete reaction, \( (p = 1) \), theoretical curves have been generated using three different rate constant values (Figure 18). The experimental \( \langle M_n \rangle \) values for poly(amic acid) synthesized in NMP and THF with \( r = 0.96906 \), and \( C_0 = 0.20584 \) are shown on the same figure. The experimental results for the poly(amic acid) synthesized in NMP plateau at a much lower \( \langle M_n \rangle \) than 20,000 g/mole, closer to 7,000 g/mole. This could be caused by one of three possibilities. The first is that the reactant ratio used was less than 0.96906. This could occur due to impure monomers, or loss of monomer during transfer to reaction flask. The second possibility is that the small amount of cyclic due to relatively dilute monomer concentration caused the \( \langle M_n \rangle \) values to be low. The low molecular weight peaks observed in the SEC chromatograms which are suspected to be cyclic oligomers could not be separated in the calculation of the MWD of the poly(amic acid) synthesized in NMP due to their close proximity to

146
Figure 3-18. Comparison of Theoretical vs. Empirical $<M_n>$ Increase with Time
(Experimental Values Without LMW Component)
the main higher molecular weight polymer peak. The third possibility is that the actual molecular weight of the poly(amic acid) in the NMP solvent decreased upon precipitation in the water during recovery. This third possibility is supported by the fact that the molecular weight of a sample of poly(amic acid) in NMP solution from the same reaction had a significantly higher molecular weight distribution. It is likely that the second and third possibilities described are contributors to the lower than expected plateau value for the molecular weights of the poly(amic acid) synthesized in NMP. However the time required to reach the plateau molecular weight of roughly 8 hours is relevant, and indicates that the rate constant for the overall reaction of bis A-dianhydride with meta-phenylene diamine in NMP is relatively small.

In contrast to the poly(amic acid) synthesized in NMP, the poly(amic acid) synthesized in THF reached high molecular weight quickly, within 20 minutes. The poly(amic acid)s synthesized in THF and analyzed by SEC also showed a low-molecular weight peak, possibly due to cyclic oligomer. However, in the case of these samples, sufficient resolution was achieved in the analysis to calculate the molecular weight distributions both with and without the low molecular weight peaks. The values calculated without the low molecular weight peaks are shown on Figure 3-17.

One important detail to note is that upon removing the THF slowly from the bulk reaction solution by sweeping nitrogen across the shallow teflon container, the resultant molecular weight of the poly(amic acid) was increased significantly (<Mₐ> = 16,800 g/mole, <Mₘ> = 28,500 g/mole) over that measured from the final sample taken during the course of the reaction where the solvent was evaporated quickly (<Mₐ> = 14,900 g/mole, <Mₘ> = 23,700 g/mole).
may be explained by a linear to cyclic equilibrium. Upon concentrating the solution the equilibrium shifts toward higher molecular weight linear species. When the solvent was removed rapidly, there was insufficient time for conversion of the cyclic to linear species.

When determining the weight percentage of THF in the poly(amic acid) synthesized in THF, it was found that regardless of how long the poly(amic acid) was dried at 20°C under vacuum, approximately 19 wt. % of residual THF remained. The theoretical amount of THF in the poly(amic acid) in the case of 1 THF per 1 -COOH group is 18.7 wt. %. Similar stoichiometric association complexes are known to form between poly(amic acid)s and amide solvents such DMAc or NMP \(^{43,59}\). Complexes like these may help to drive the equilibrium amidization reaction to completion, thus offering an explanation for the rapid rate of amidization for bis-A dianhydride with m-phenylene diamine in THF.

Poly(amic acid) salts with systematically varied cations were prepared from a 16,000 g/mole \(<M_n>\) poly(amic acid) in methanol or water, dried, and their solubilities in water and methanol were compared at a concentration of 4.7% w/v of poly(amic acid) in solvent or 0.15 M based on [-COO\(^-\)]. All of the poly(amic acid) salts were soluble in methanol. Water solubility is considered an important processing advantage since this would allow the salts to be applied as fiber sizings from aqueous solutions, or to be incorporated into waterborne resins as thermoplastic toughening agents for thermosets. A 10 mole percent excess of base was used (with the exception of the triethylamine case) because previous studies have suggested that small excesses of base should yield poly(amic acid) salt solutions where the polyelectrolytes are more
hydrolytically stable\textsuperscript{42}. Results from the solubility study are presented in Table 3-3. Interestingly, the solubilities of the salts followed a trend consistent with polyelectrolyte theory\textsuperscript{60}. Hydrated diameters for the alkyl ammonium ions have been calculated based on ionic mobilities (Table 3-4) \textsuperscript{61}. As the tetralkylammonium counterion size was increased from tetramethyl- to tetaethyl- and tetrapropylammonium, the salts became soluble in water (produced clear aqueous solutions). This is probably because the carboxylate charges are increasingly less shielded with the larger cations, and, hence, the polyelectrolyte becomes more soluble. However, a hydrophobic effect apparently overwhelms the deshielding effect for tetrabutylammonium cations, and water solubility again decreases. Although it is difficult to directly compare the shielding effect for the triethylammonium poly(amic acid) salts, it is important to note that although this material swelled appreciably, it was essentially water insoluble. However, an analogous triethylammonium salt was prepared using an 8,800 g/mole $<M_n>$ poly(amic acid), and this lower molecular weight polymer did completely dissolve in water. This suggests that molecular weight may play a significant role in poly(amic acid) salt solubility. It is suggested that this point warrants further investigation at a later time.

Melt imidization conditions for the poly(amic acid) salts were investigated by conducting reactions at two temperatures, 250°C and 300°C, each for 30 minutes. To achieve quantitatively imidized polymers within a reasonable time, it is necessary to reach temperatures at least 20-30°C above the glass transition temperature ($T_g$ Ultem Polyimide $\sim$ 220°C). At temperatures of 300°C and higher, crosslinking of the polyimide may also occur. The percentage of weight loss which occurred during these imidization reactions, and the glass transition
Table 3-3. Solubilities of Poly(amic acid) Salts

<table>
<thead>
<tr>
<th>Polyamic acid Salt (preparation solvent)</th>
<th>Conc = 0.15M [-COO(^-)]</th>
<th>Conc = 0.15M [-COO(^-)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetramethylammonium (MeOH)</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>Tetraethylammonium (H(_2)O)</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>Tetraethylammonium (MeOH)</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>Tetrapropylammonium (H(_2)O)</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>Tetrabutylammonium (MeOH)</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>Triethylamine (MeOH)</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>&lt;Mn&gt; of Poly(amic acid)</td>
<td>&lt;Mn&gt;=16,000 g/mole</td>
<td>&lt;Mn&gt;=8,800 g/mole</td>
</tr>
</tbody>
</table>
Table 3-4. Hydrated Ionic Diameters Calculated from Ionic Mobilities\textsuperscript{61}

<table>
<thead>
<tr>
<th>Organic Ion</th>
<th>Name</th>
<th>Hydrated Diameter Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CH\textsubscript{3})\textsubscript{4}N\textsuperscript{+}</td>
<td>Tetramethylammonium</td>
<td>4.5</td>
</tr>
<tr>
<td>(C\textsubscript{2}H\textsubscript{5})\textsubscript{3}NH\textsuperscript{+}</td>
<td>Triethylammonium</td>
<td>5</td>
</tr>
<tr>
<td>(C\textsubscript{2}H\textsubscript{5})\textsubscript{4}N\textsuperscript{+}</td>
<td>Tetraethylammonium</td>
<td>6</td>
</tr>
<tr>
<td>(C\textsubscript{3}H\textsubscript{7})\textsubscript{3}NH\textsuperscript{+}</td>
<td>Tripropylammonium</td>
<td>7</td>
</tr>
<tr>
<td>(C\textsubscript{3}H\textsubscript{7})\textsubscript{4}N\textsuperscript{+}</td>
<td>Tetrapropylammonium</td>
<td>8</td>
</tr>
</tbody>
</table>
temperatures of the polyimides are compared in Table 3-5. The experimental weight losses have been corrected for the small amounts of solvent which were retained in the poly(amic acid) salts (and in the PAA control). For all cases, the weight losses closely matched the theoretically expected values, indicating that the conversion to polyimide quantitatively occurred with the thermal treatment used. The appearance of the polyimides prepared at 250°C differed from those formed at 300°C (Figures 3-19 - 3-22). The 250°C samples formed foams with varying densities, suggesting that the melt viscosities at 250°C were sufficiently high to inhibit efficient flow during the process. The foam formed from the triethylammonium poly(amic acid) salt was qualitatively the least dense, yet appeared to have the best mechanical properties. The polyimides formed at 300°C did not retain any foamed structure, and exhibited significant viscous flow during the process. It is clear that the rheology of these melts, with respect to the particular imidization conditions, warrants further investigation.

For linear polyimides with molecular weights in the 5000 - 20,000 g/mole $<M_n>$ range, it is well known that the Tg's increase with $<M_n>$. The glass transition temperatures of the polyimides prepared from the poly(amic acid) salts were compared with the "control" material imidized directly from the poly(amic acid). It was reasoned that this data, in conjunction with SEC results, would provide an indication of whether the molecular weight of the original poly(amic acid) could be retained in the polyimides following salt formation in water (or methanol), subsequent drying, then imidization from the salts. By differential scanning calorimetry no crystalline melting endotherms were observed. In general, Tg's of the polyimides prepared at 300°C were about 6°C higher than of those imidized at 250°C. The polyimides exhibiting the highest
Table 3-5. Wt. Loss on Imidization, and Thermal Properties of Polyimides from Poly(amic acid) Salts

<table>
<thead>
<tr>
<th>Polyamic acid Salt</th>
<th>5% wt. Loss(^1)</th>
<th>T °C 30min</th>
<th>% wt. Loss(^2)</th>
<th>Theor % Wt. Loss</th>
<th>Tg °C(^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyamic acid Control</td>
<td>522°C</td>
<td>250</td>
<td>7.8</td>
<td>5.7</td>
<td>207</td>
</tr>
<tr>
<td></td>
<td></td>
<td>300</td>
<td>6.6</td>
<td>5.7</td>
<td>213</td>
</tr>
<tr>
<td>Tetramethylammonium</td>
<td>395°C</td>
<td>250</td>
<td>22.9</td>
<td>23.5</td>
<td>193</td>
</tr>
<tr>
<td>(MeOH)</td>
<td></td>
<td>300</td>
<td>24.4</td>
<td>23.5</td>
<td>190</td>
</tr>
<tr>
<td>Tetraethylammonium</td>
<td>506°C</td>
<td>250</td>
<td>33.9</td>
<td>33.2</td>
<td>199</td>
</tr>
<tr>
<td>(H(_2)O)</td>
<td></td>
<td>300</td>
<td>33.8</td>
<td>33.2</td>
<td>204</td>
</tr>
<tr>
<td>Tetraethylammonium</td>
<td>495°C</td>
<td>250</td>
<td>34.2</td>
<td>33.2</td>
<td>203</td>
</tr>
<tr>
<td>(MeOH)</td>
<td></td>
<td>300</td>
<td>34.4</td>
<td>33.2</td>
<td>211</td>
</tr>
<tr>
<td>Tetrapropylammonium</td>
<td>503°C</td>
<td>250</td>
<td>41.1</td>
<td>40.7</td>
<td>198</td>
</tr>
<tr>
<td>(H(_2)O)</td>
<td></td>
<td>300</td>
<td>41.1</td>
<td>40.7</td>
<td>198</td>
</tr>
<tr>
<td>Tetrabutylammonium</td>
<td>444°C</td>
<td>250</td>
<td>47.1</td>
<td>46.7</td>
<td>189</td>
</tr>
<tr>
<td>(MeOH)</td>
<td></td>
<td>300</td>
<td>47.7</td>
<td>46.7</td>
<td>200</td>
</tr>
<tr>
<td>Triethylamine (MeOH)</td>
<td>519°C</td>
<td>250</td>
<td>30.4</td>
<td>28.7</td>
<td>213</td>
</tr>
<tr>
<td></td>
<td></td>
<td>300</td>
<td>30.8</td>
<td>28.7</td>
<td>218</td>
</tr>
</tbody>
</table>

1) 5% wt. loss from polyimide plateau determined dynamically in air, 10°C/min.
2) % wt. loss on imidization (values corrected for residual solvent weight).
3) Tg determined by DSC, 10°C/min.
Figure 3-19 and 3-20. Photographs of Polyimides Prepared from Poly(amic acid) Salts
Figure 3-21 and 3-22. Photographs of Polyimides Prepared from Poly(amic acid) Salts
glass transition temperatures were the materials imidized from the poly(amic acid) (300°C), from the triethylammonium salts at both temperatures (the salt was prepared in methanol), and from one of the tetraethylammonium salts (from the salt prepared in methanol and imidized at 300°C). Of these higher \( T_g \) polyimides, the control material as well as both polyimides prepared from the triethylammonium salts were soluble in NMP and chloroform, whereas, by contrast, the polyimide prepared from the tetraethylammonium salt was no longer soluble. The thermal analysis data, combined with the SEC results, suggests that the polyimides prepared from the triethylammonium salts under these melt conditions have retained both their original molecular weights and that crosslinking did not occur. In contrast, none of the polyimides prepared from the tetralkylammonium salts had those characteristics.

As alluded to above, the weight average and number average molecular weights of the polyimides (Table 3-6) support these same observations. It should be noted that the average molecular weights reported in Table 3-6 were calculated neglecting a small low molecular weight peak discussed previously. The highest polyimide number average molecular weights of 16,300 g/mole and 15,000 g/mole corresponded to the triethylammonium salts prepared in methanol, then imidized at 300°C and 250°C respectively. Partially insoluble gel's were noted for some of the polyimide samples, by dissolving the polyimides in chloroform. The polydispersities, \( (M_W/M_N) \), were above the most probable value of 2.0 as crosslinking began to occur in the polyimides imidized at 300°C.

According to free volume theory, free volume around the polymer chain ends is greater than that along the polymer chain, due to the higher mobility of
Table 3-6. Molecular Weights of Polyimides from Poly(amic acid) Salts

<table>
<thead>
<tr>
<th>Polyamic acid Salt</th>
<th>T °C 30 min</th>
<th>&lt;Mn&gt; g/mole</th>
<th>&lt;Mw&gt; g/mole</th>
<th>&lt;Mw&gt; / &lt;Mn&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyamic acid Control</td>
<td>250</td>
<td>10,400</td>
<td>19,800</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>13,200</td>
<td>28,600</td>
<td>2.2</td>
</tr>
<tr>
<td>Tetramethylammonium (MeOH)</td>
<td>250</td>
<td>8,990</td>
<td>16,200</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>7,500</td>
<td>20,000</td>
<td>2.7 slight gel</td>
</tr>
<tr>
<td>Tetraethylammonium (H2O)</td>
<td>250</td>
<td>8,970</td>
<td>17,300</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>11,500</td>
<td>73,400</td>
<td>6.4 slight gel</td>
</tr>
<tr>
<td>Tetraethylammonium (MeOH)</td>
<td>250</td>
<td>9,500</td>
<td>21,300</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>gel</td>
<td>gel</td>
<td>gel</td>
</tr>
<tr>
<td>Tetrapropylammonium (H2O)</td>
<td>250</td>
<td>8,910</td>
<td>15,800</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>9,840</td>
<td>19,400</td>
<td>2.0</td>
</tr>
<tr>
<td>Tetrabutylammonium (MeOH)</td>
<td>250</td>
<td>8,490</td>
<td>14,700</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>10,100</td>
<td>21,900</td>
<td>2.2 slight gel</td>
</tr>
<tr>
<td>Triethylamine (MeOH)</td>
<td>250</td>
<td>15,000</td>
<td>28,800</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>16,300</td>
<td>32,600</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Molecular weights determined by SEC, (values not including small low molecular weight peak).
the chain ends. It follows from free-volume theory that $T_g = T_g^{\infty} - c/<M_n>^{62}$. This relationship was shown empirically by Fox and Flory $^{63}$. In Figure 3-23 the glass transition temperatures of the polyimides formed from the poly(amic acid) salts are plotted versus the polyimide $1/<M_n>$ values. The number average molecular weight values used were not corrected in this case for the small low molecular weight component, as this low molecular weight component should contribute significantly to the glass transition temperature value. $T_g^{\infty}$ is the value of the glass transition temperature for a linear polymer with infinitely few chain ends, or infinitely high $<M_n>$. By extrapolating the plot of $T_g$ versus $1/<M_n>$ to infinite molecular weight, the $T_g^{\infty}$ value for the Ultem™ type poly(etherimide) was determined. 237°C is calculated to be the $T_g^{\infty}$ value for the Ultem™ type poly(etherimide).

Each of the polyimides was potentiometrically titrated with hydrobromic acid in glacial acetic acid to detect residual aromatic amine endgroups which may have resulted from hydrolysis or methanolysis during salt formation or imidization. Theoretically, for a molecular weight controlled poly(imide) with non-reactive endgroups there should be no amine functionality. In Table 3-7 the results of the potentiometric titration of the imidized poly(amic acid) salts for aromatic amine content are given. Theoretically, for a molecular weight controlled poly(imide) with non-reactive endgroups there should be no aromatic amine functionality present in the form of endgroups. However, if chain scission occurs through a hydrolysis mechanism, aromatic amine end-groups could have formed. The quantity of aromatic amine endgroups is related to the degree of hydrolysis. The results are provided in terms of number of imide moieties per aromatic amine functionalities, with 2 imide moieties per polymer

159
Figure 3-23. Tg vs. $1/<M_n>$ for Poly(imide)s

$y = 237.34 - 2.8299e+5x \quad R^2 = 0.946$
### Table 3-7. Potentiometric Titration of Imidized Poly(amic acid) Salts with HBr for Aromatic -NH₂

<table>
<thead>
<tr>
<th>Polyamic acid Salt</th>
<th>T °C 30min</th>
<th>&lt;M₉&gt;₁ g/mole</th>
<th>imide/NH₂²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyamic acid Control</td>
<td>250</td>
<td>9,300</td>
<td>&gt;115</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>10,700</td>
<td>&gt;115</td>
</tr>
<tr>
<td>Tetramethylammonium (MeOH)</td>
<td>250</td>
<td>6,510</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>6,040</td>
<td>14</td>
</tr>
<tr>
<td>Tetraethylammonium (H₂O)</td>
<td>250</td>
<td>7,550</td>
<td>56</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>8,270</td>
<td>&gt;115</td>
</tr>
<tr>
<td>Tetraethylammonium (MeOH)</td>
<td>250</td>
<td>8,150</td>
<td>112</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>gel</td>
<td>&gt;115</td>
</tr>
<tr>
<td>Tetrabutylammonium (H₂O)</td>
<td>250</td>
<td>6,110</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>8,150</td>
<td>30</td>
</tr>
<tr>
<td>Triethylamine (MeOH)</td>
<td>250</td>
<td>13,200</td>
<td>&gt;115</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>13,400</td>
<td>&gt;115</td>
</tr>
</tbody>
</table>

(1) <M₉>₁ values for polyimide samples imidized from poly(amic acid) salts were determined by SEC (includes the small low molecular weight "tail peak").

(2) Moles of imide moeity per mole of amine moeity. The limit of detection for the determination was 115 moles imide per mole amine.

(3) Observed when polyimide was dissolved in chloroform.
repeat unit. For a perfectly non-functional endcapped poly(amide) this number will be infinite. With the detection limits utilized in the titration experiment, values of up to 115 imide groups per amine group could be calculated. Since this was the detection limit, the actual values may be higher. The polyimides formed from the control poly(amic acid), and from the triethylammonium poly(amic acid) salts had low aromatic amine content (undetectable), at both the 250°C and 300°C imidization temperatures. For these two polyimides, the cure occurred without any cross-linking, as evidenced by the polyimide product's solubility, and most probable molecular weight distribution of 2. In the case of the polyimides formed from the tetraethylammonium poly(amic acid) salt the titration results also indicated low levels of aromatic amine, but these samples formed cross-linked materials upon imidization at 300°C. The polyimides formed from the tetramethylammonium and tetrabutylammonium poly(amic acid) salts showed high levels of aromatic amine by titration. No strong correlation was apparent between the titration results, and the <Mₙ> results obtained by Size Exclusion Chromatography.

Poly(amic acid)s are known to be hydrolytically unstable, with a mechanism of hydrolysis involving the acid catalyzed back reaction to anhydride and amine. The rate of this back reaction increases at elevated temperatures resulting in a detectable anhydride peak by infrared spectroscopy. Even if water is not present during the initial poly(amic acid) formation, when the poly(amic acid) is thermally imidized, the water which is a product of the imidization may react with the anhydride to cause hydrolysis. The product of the hydrolysis reaction is a dicarboxylic acid and an aromatic amine. With sufficient thermal energy and chain mobility, amidization can occur, followed by
imidization. Therefore, even though chain scission may occur in a poly(amic acid) during processing to a polyimide, chain rehealing can occur resulting in high or controlled molecular weight polyimide. In the case of a poly(amic acid) salt, if hydrolysis occurs during preparation of the salt by reaction of the base with the poly(amic acid), or after the poly(amic acid) salt is prepared, chain rehealing can theoretically occur during thermal treatment to imidize poly(amic acid) salt. This may be critical to achieving high molecular weight or controlled molecular weight polyimide. Chain healing has been observed for poly(amic acid) salts imidized at 300°C for 30 minutes (Table 3-8). Two slightly hydrolyzed poly(amic acid) samples were used, one synthesized in THF (and containing residual quantities of THF), and the other synthesized in NMP. The original $<M_n>$'s for both poly(amic acid)'s were about 15,000 g/mole. The poly(amic acid)'s were slightly hydrolyzed during storage at room temperature with occasional exposure to laboratory air. Salts were prepared utilizing a 1/1 stoichiometry of triethylamine to carboxylic acid. Samples of the poly(amic acid)'s and the poly(amic acid) salts were imidized at 300°C for 30 minutes. All samples were analyzed in NMP/P₂O₅ by SEC utilizing Universal Calibration techniques.

The poly(amic acid) salts in this study imidize by different mechanisms, depending on which counterion is present. It is reasonable to suggest that a poly(amic acid) salt does not imidize directly from the salt form. This is due to the inherent low reactivity of a carboxylate carbonyl toward nucleophilic acyl substitution on the carbonyl carbon. Different imidization mechanisms are likely depending upon which cation is associated with carboxylate anion. For the case of the tetra ethyl, propyl, and butyl tetraalkylammonium poly(amic acid)
Table 3-8. Chain Rehealing During Imidization of Poly(amic acid) Salts (Molecular Weights by SEC in NMP/P_2O_5.)

<table>
<thead>
<tr>
<th></th>
<th>PAA THF^1</th>
<th>PAA THF^2</th>
<th>1/1TEA PAAS^3</th>
<th>PAA NMP^4</th>
<th>PAA NMP^5</th>
<th>1/1TEA PAAS^6</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;M_n&gt; g/mole</td>
<td>8,840</td>
<td>12,400</td>
<td>15,800</td>
<td>9,620</td>
<td>20,200</td>
<td>13,000</td>
</tr>
<tr>
<td>&lt;M_w&gt; g/mole</td>
<td>14,400</td>
<td>24,600</td>
<td>32,500</td>
<td>19,000</td>
<td>47,000</td>
<td>30,300</td>
</tr>
<tr>
<td>&lt;M_z&gt; g/mole</td>
<td>20,700</td>
<td>41,200</td>
<td>53,100</td>
<td>36,100</td>
<td>82,800</td>
<td>64,700</td>
</tr>
</tbody>
</table>

(1) Poly(amic acid) synthesized in THF.
(2) Poly(amic acid) synthesized in THF imidized at 300°C for 30 minutes.
(3) Polyimide from poly(amic acid) salt [prepared in H_2O at 0.15M [-COO^-].
poly(amic acid) synthesized in THF].

(4) Poly(amic acid) synthesized in NMP.
(5) Poly(amic acid) synthesized in NMP imidized at 300°C for 30 minutes.
(6) Polyimide from poly(amic acid) salt [prepared in H_2O at 0.15M [-COO^-].
poly(amic acid) synthesized in NMP].
salts we suggest that two feasible imidization routes exist. In the one route, imidization can be preceded by a Hoffman elimination reaction involving abstraction by the carboxylate of the proton β to the nitrogen to form the acid, ethylene, and a trialkylamine (Figure 3-24, equation 1a). After the poly(amic acid) is formed it may subsequently imidize with the loss of water, or it may re-protonate the trialkylamine product after which further Hoffman type elimination reactions are possible. The second possibility is the $S_N2$ type nucleophilic substitution reaction where the carboxylate anion displaces an alkyl group from the tetraalkylammonium carbocation to form an ester of poly(amic acid) and trialkylamine (Figure 3-24, equation 1b). The poly(amic ester) subsequently imidizes with the loss of alcohol. For tetramethylammonium poly(amic acid) salt, the Hoffman elimination route is not possible due to the absence of a proton β to the nitrogen. In this case only the $S_N2$ substitution may occur, with the carboxylate anion displacing a methyl group from the tetramethylammonium carbocation, resulting in trimethylamine and the methyl amic acid ester. Alkyl amic acid esters have been shown in several studies to imidize readily, though at higher temperatures than the corresponding poly(amic acid)s $^{35,37,64-66}$. In the case of the triethylamine poly(amic acid) salt, an equilibrium non-covalent bond breaking route is possible where the carboxylate anion can simply abstract the proton associated with the protonated triethylamine, to form the amic acid and triethylamine in it's non-protonated form. It is also possible, but less likely for the triethylamine poly(amic acid) salt to imidize via the higher energy Hoffman Elimination type reaction. The trialkylamines formed during the conversion to acid may act in situ to facilitate the imidization, by acting in a dual

165
Tetraethylammonium Salt of PAA

Hoffman Elimination

Nucleophilic Substitution

Tetramethylammonium Salt of PAA

Nucleophilic Substitution

Triethylammonium Salt of PAA

Equilibration

Figure 3-24 Speculated Imidization Mechanisms for Poly(amic acid) Salts
fashion as plasticizing agents in a similar fashion to NMP \(^6\) and also as rate increasing catalysts for imidization \(^{43}\).

Chemical species detected using mass spectrometry to analyze the effluents resulting from imidization of the poly(amic acid) salts are listed in Table 3-9.

**Table 3-9. Species detected by GC-MS Analysis of Imidization Products**

<table>
<thead>
<tr>
<th>Poly(amic acid) Salt</th>
<th>Species Detected</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetramethylammonium</td>
<td>trimethylamine, methanol</td>
</tr>
<tr>
<td>Tetraethylammonium</td>
<td>triethylamine, ethanol</td>
</tr>
<tr>
<td>Tetrapropylammonium</td>
<td>propanol</td>
</tr>
<tr>
<td>Tetrabutylammonium</td>
<td>butanol</td>
</tr>
<tr>
<td>Triethylammonium</td>
<td>triethylamine</td>
</tr>
</tbody>
</table>

The GC-MS analyses suggest that the nucleophilic substitution imidization route is the predominant route of imidization for the quaternary ammonium poly(amic acid) salts. The alkene byproducts of Hoffman type elimination reactions were not observed in the GC-MS experiments. Apparently the carboxylate anion is not a strong enough base to participate in the proton abstraction step in an E2 type elimination, but is an efficient nucleophile (at 250°C-300°C) for dealkylation of the quaternary ammonium ion to form the amic ester and tertiary amine. Similar dealkylation reactions by carboxylate ions have been reported previously. In a British study, dealkylation of quaternary
ammonium salts by the acetate anion was shown to proceed at temperatures of 60-140°C in solvents with low dielectric constants\textsuperscript{68}. The GC-MS experiments confirmed that the simple proton transfer mechanism for the triethylamine poly(amic acid) salt is predominant, as triethylamine was the only effluent detected. The results from this research are similar to a study of imidization of poly(amic esters)\textsuperscript{34}. The t-butyl ester imidized by first forming the amic acid (with simultaneous formation of isobutene) resulting in rapid imidization and high molecular weights. In the same study poly(amic n-alkyl ester), imidized directly with release of n-alcohols, with slower rates and producing lower molecular weights\textsuperscript{34}. The combined results of these studies suggest that when facile routes to the amic acid exist for poly(amic acid) derivatives, rapid imidization with high degrees of molecular weight retention may result.

The dynamic thermal behavior of the poly(amic acid) salts was determined in air by measuring weight loss while heating at 10°C/minute using a DuPont Thermogravimetric Analyzer Model 951. Sample thermograms are shown in Figure 3-25. The first weight losses were observed at temperatures of about 200°C corresponding to imidization of the poly(amic acid) salts. Quantitative weight losses were not determined using the DuPont Thermogravimetric Analyzer as the small sample sizes (3 mg) would have resulted in low precision. However, quantitative weight losses upon imidization were determined by using larger samples and imidizing in an oven isothermally at 250°C or 300°C for 30 minutes. After correcting the values for the weight % solvent contained in the poly(amic acid) salts, the experimental values were in all cases within 1% of the theoretical values indicating that quantitative imidization had occurred (Table 3-5). The second weight losses observed for
Figure 3-25. Dynamic Thermal Stability of Poly(amic acid) Salts in Air.

(10°C/min)
all of the poly(amic acid) salts, subsequent to that occurring upon imidization were due to degradation of the polyimides. The 5% weight loss temperature from the polyimide plateau was calculated for all of the poly(amic acid) salts (Table 3-5). This value is representative of the dynamic thermal stability of the polyimide resulting from heating the precursor poly(amic acid) salt in air. The polyimides resulting from the control poly(amic acid) and the triethylammonium poly(amic acid) salt showed the best stabilities, with a 5% wt. loss temperature value for each of ≈ 520°C. The polyimides resulting from the tetraethylammonium and tetrapropylammonium polyamic acid salts each displayed 5% wt. loss values of ≈ 500°C. The materials imidized from the tetrabutylammonium and tetramethylammonium salts showed decreased 5% wt. loss temperature values of 444°C and 395°C respectively.

3.6. CONCLUSIONS

Controlled molecular weight polyimides can be synthesized via triethylammonium polyamic acid salts. The mechanism of imidization and the properties of polyimides derived from poly(amic acid) salt precursors are dependent on the identity of the counterion. Synthesis of Ultem™ type poly(amic acid) precursors in THF proceeds more rapidly then in N-methylpyrrolidinone. The THF forms a stoichiometric complex with the carboxylic acid groups of the poly(amic acid) resulting in a residual 18.7 wt. % THF in the poly(amic acid) upon drying.
3.7. RECOMMENDATIONS FOR FUTURE WORK

In view of the finding that the trialkylammonium salt of the Ultem™ type poly(amic acid) thermally imidizes to molecular weight controlled polyimides, but the water solubility of the triethylammonium salt of poly(amic acid) is low for high molecular weight poly(amic acid) precursors, a study should be undertaken involving the preparation, solubility, and imidization of molecular weight controlled polyimides from tripropylammonium poly(amic acid) salts. The hydrated ionic diameter of the tripropylammonium ion \(^6\) should provide good water solubility for the poly(amic acid) salts, and retain the chemistry of the triethylammonium salts which provide for excellent molecular weight control. Because polyimides are used in electrical applications where low dielectric constant is important, the dielectric properties of the imidized poly(amic acid) salts should be studied, and compared to imidized control poly(amic acid)s. Other important areas of future research include extension of this work to other higher performance polyimide systems, and the study of controlled molecular weight polyimides with functional endgroups via poly(amic acid) salt precursors.

3.8. REFERENCES


(24) Young, P. R.; Chang, A. C. *SAMPE Prepr.* 1985, 30, 889.


(65) Cotts, P. M.; Volksen, W. Polymers News 1990, 15, 106.


Chapter 4  Fine (Sub-μm) Poly(ether ether ketone) Powders

4.1. INTRODUCTION

The physical form of polymers is often important for carrying out subsequent processing operations. For example, fine powders are desirable for molding and sintering compounds because they consolidate readily to produce void free components due to the thermodynamic driving force to reduce the surface free energy \(^1\). The objective of this project was to prepare fine polymeric particulates suitable for processing into fiber reinforced polymer matrix composites. Micron size particles of poly(ether ether ketone) (PEEK) were prepared by rapidly quenching solutions of these materials. PEEK powder of average particle diameter 50 μm was dissolved at temperatures near the PEEK melting point in a mixture of terphenyl and quaterphenyl; then the solution was quenched to a temperature between the Tg and Tm (≈225°C) by adding a room temperature eutectic mixture of diphenyl ether and biphenyl. A supersaturated, metastable solution of PEEK resulted causing rapid nucleation. Fine PEEK particles rapidly crystallized from this solution. The average particle size was measured using transmission electron microscopy, atomic force microscopy, and by light scattering of aqueous suspensions which had been fractionated by centrifugation. The average particle diameter was about 0.6 μm. Three dimensional photomicrographs obtained via atomic force microscopy showed some agglomerates in the suspensions.

Poly(ether ether ketone) (PEEK) (Figure 4-1) is a semi-crystalline thermoplastic with excellent thermal stability, good mechanical properties at
elevated temperatures, and good solvent resistance \(2^\cdot 4\). It has a glass transition temperature of \(\approx 143^\circ C\) and a melting point of \(\approx 334^\circ C\). These properties make PEEK attractive as a high performance matrix for carbon fiber reinforced composites, and also for molded objects when particularly good thermo-oxidative stability is required. Fine particulates of these semi-crystalline poly(ether ketone)s are desirable for both composite powder processing, and as high performance molding and sintering compounds.

\[
\begin{align*}
&\text{Figure 4-1. Poly(ether ether ketone) (PEEK)}
\end{align*}
\]

Researchers from Virginia Tech recently reported a process for preparing submicron diameter PEEK particles by rapidly hydrolyzing a soluble precursor polymer, poly(ether ether ketimine), to PEEK \(^5\). Supersaturated PEEK solutions formed, and the polymer rapidly nucleated and crystallized from the solutions in the form of small particles. The project discussed in this chapter explored a complementary "rapid quenching" method for generating small PEEK particles via supersaturated PEEK solutions. PEEK is dissolved at temperatures near its melting point in a mixture of terphenyl and quaterphenyl; then the solution is quenched to a temperature between PEEK's \(T_g\) and \(T_m\) (\(\approx 225^\circ C\)) by adding a room temperature mixture of diphenyl ether and biphenyl. The rapid drop in temperature also creates a supersaturated PEEK solution, and fine PEEK
particles rapidly form. This provides a route to small, semi-crystalline powders without any need to separately synthesize an amorphous precursor polymer.

4.2. EXPERIMENTAL

4.2.1 Materials and Apparatus

PEEK powder (Victrix PEEK 450PF, melt viscosity 380-500 Pa·sec at 400°C, and 1000 sec⁻¹, average particle diameter 50 μm, all particles < 104 μm diameter) was purchased from Victrix USA, West Chester, PA. Two heat transfer fluids were used to prepare and precipitate the PEEK powders; Therminol 75™ was purchased from Monsanto Chemicals, and Therminol VP-1™, was generously donated by Monsanto. Therminol 75™ is a mixture of terphenyl and quaterphenyl isomers (Figure 4-2) with 90% of the mixture boiling at 340°C/50 mm Hg, and is a soft yellowish solid at room temperature (melting point 40-70°C). Therminol VP-1™ is a eutectic mixture of biphenyl and diphenyl ether (73.5 wt.% diphenyl ether) (Figure 4-3) with a boiling point of 257°C at 760 mm Hg. It is a clear liquid at room temperature. Toluene (Ashland Chemicals, Reagent Grade) and THF (Fisher, Reagent Grade), used as extraction solvents to remove residual heat transfer fluids after particle formation, were used as received. The reaction vessel consisted of a 50 L roundbottom glass flask equipped with a heating mantle, a modified Turbomixer stirring assembly, thermocouple, and nitrogen inlet and outlet. The stirring assembly consisted of a 6” oval, variable pitch coiled spring, mounted perpendicular with respect to the shaft axis to the end of a 3/4” diameter shaft. A 6” marine propeller was
Figure 4-2. Therminol VP1: Eutectic Mixture of Diphenyl and Diphenyl Ether

Figure 4-3. Therminol 75: Mixture of Terphenyl and Quaterphenyl Isomers
mounted 7" above the coil. All materials used for the stirring assembly were 316 SS.

4.2.2 Particulate Formation

Thermolin 75™ (15.5 kg) was charged to the flask and heated to 80°C to melt the solvent. PEEK powder (2.15 kg) was added to the fluid, and the sides of the flask were rinsed with 2 kg Thermolin VP-1™. The mixture was stirred at 300 rpm and heated to 340°C for four hours under a nitrogen atmosphere to dissolve the polymer; then the heating mantle was turned off, and the temperature was allowed to drop to 330°C. A clear, dark solution of PEEK in Thermolin 75™ resulted. The stirring rate was increased to 1500 rpm, and 16 kg of Thermolin VP-1™ was added at 25°C over 25 seconds to produce a PEEK solids content of = 6 wt. percent. The temperature of the mixture fell to 225°C. The PEEK particles precipitated almost instantaneously after about 12 kg of the Thermolin VP-1™ had been added. It should be noted that stirring was inefficient after particle precipitation, but this did not cause severe aggregation of the particles. The mixture was allowed to cool to 100°C, then diluted with 16 L toluene. The resultant slurry was subdivided into two identical flasks to facilitate stirring. An additional 16 L of toluene was added to each of the flasks, and the slurries were stirred overnight at room temperature.

To remove the major portion of the heating fluids, the aggregates of PEEK powder were isolated by vacuum filtration in a Büchner funnel, resuspended in toluene (60 L total) and stirred under nitrogen at 100°C for 12 hours, filtered, resuspended in THF (60 L total) and refluxed for ≈12 hours, filtered again and washed with hot deionized water twice, then suspended in deionized water. Note that, in the absence of a suitable suspension stabilizer,
the small PEEK particles form a highly viscous suspension in water. Gas chromatography was used to monitor removal of this major portion of the heating fluid from the particles. Both residual Therminol VP-1™ and Therminol 75™ remained in the THF effluent after filtration.

To establish the approximate concentration of the suspension, 200 mL of the aqueous PEEK suspension was diluted with 200 mL of THF, filtered in a Büchner funnel, and washed with an additional 100 mL of THF. These particles were air dried for 2 days, then dried at 40°C in vacuo for ≈ 48 hours to obtain 13.3 g of relatively dry material. Experience has shown that if the small PEEK particles are dried at an elevated temperature, they irreversibly flocculate.

4.2.3 Purification of the PEEK powder

Approximately 13.3 grams of isolated PEEK particles (dried at 40°C) were refluxed in 290 mL THF (b.p. 67°C) for 24 hours, then cooled to 20°C. A sample of the supernatant THF was removed for analysis by GC-MS (gas chromatography - mass spectroscopy) (Sample 1, Table 4-1). The PEEK was placed in a 43 mm x 123 mm cellulose extraction thimble and Soxhlet extracted for 24 hours. The PEEK was refluxed again in 290 mL fresh THF for 24 hrs., cooled, and a second sample of the supernatant THF was withdrawn (Sample 2, Table 4-1). The PEEK was again soxhlet extracted in THF for 24 hours., then refluxed in fresh THF (290 mL) for 24 additional hours, and a third sample of the supernatant was removed for analysis (Sample 3, Table 4-1). The sample was soxhlet extracted for 24 hours a final time.
4.2.4  Characterization

4.2.4.1  Gas Chromatography/Mass Spectrometry

A Fisons GC 8060 coupled with a Fisons VG QUATTRO Mass Spectrometer was used to analyze the samples. The DB-5MS column, 15 meters long, 0.25 mm i.d., with a 0.25 μm film was purchased from J & W Scientific. A 2 minute solvent delay was used, and the gas chromatograph column temperature was ramped from 50°C to 300°C at a heating rate of 10°C/minute. Helium was used as the mobile phase, at a flow rate of 1 mL/min. The pressure at the column head was 5 psi. A 1 μL sample volume was used. Note that because no internal standard was used in this analysis, the error in delivering the 1 μL sample becomes the major error in this analysis. This error is estimated to be ± 10%.

Samples of each of the heating fluid mixtures were analyzed by GC-MS to identify peaks from the heating fluids. 20.9 mg of the biphenyl-diphenyl ether eutectic fluid was diluted to 50.0 mL with THF and 20.5 mg of the terphenyl-quaterphenyl fluid was diluted to 50.0 mL with THF. One μL aliquots of each standard were injected into the GC-Mass Spectrometer.

4.2.4.2  Thermal Analysis

Differential scanning calorimetry was conducted on a Perkin-Elmer Series 7 thermal analyzer under a nitrogen purge at a heating rate of 10°C per min. All reported transitions are from a second heating scan. Thermogravimetric analysis was conducted on a Perkin-Elmer Series 7 thermal analyzer under an air purge at a heating rate of 10°C per minute.
4.2.4.3 Particle Size Analysis

The particle size (median diameter) and particle size distribution were measured by a Shimadzu centrifugal particle size analyzer (model SA-CP3). This instrument measures the turbidity of the sedimenting suspension and utilizes Stokes law to correlate the sedimentation rate to particle size. The range of size analysis was 0.3 - 100 μm. The solvent density and viscosity as well as the density of the particle are required in the calculations. The suspension medium was water (ρ = 0.998 g/mL, η = 0.938 cP). Density of the particles was approximated by that of bulk poly(ether ether ketone) (1.3 g/mL). A dilute aqueous suspension was prepared for this analysis by adsorbing Triton X-100 stabilizer (Figure 4-4) onto the particles, then by breaking up the flocculates ultrasonically.

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3 \quad \text{C} & \quad \text{CH}_2 \quad \text{C} \\
\text{CH}_3 & \quad \text{CH}_3 \\
\end{align*}
\]

\[
\mathcal{O}(\text{CH}_2\text{CH}_2)_n \text{OH} \quad n = 10\text{avg.}
\]

Triton X-100

Figure 4-4. Triton X-100 stabilizer

The particle size was also examined by scanning transmission electron microscopy (STEM). The samples were placed on a Formvar Support Film Grid (200 mesh) obtained from Electron Microscopy Services as a dilute aqueous suspension stabilized by Triton X-100 surfactant (= 0.5% v/v), dried in air overnight, and then examined directly using a Philips 420T scanning transmission electron microscope (STEM) operating at 100 kV in the STEM mode.
The atomic force microscope (AFM) used was a Nanoscope IIIa Dimension 3000 Scanning Probe Microscope (Digital Instruments). AFM images were recorded in the tapping mode in air. Samples were prepared by placing a drop of a dilute aqueous suspension (prepared using a Triton X-100 stabilizer) on a glass substrate. After drying at room temperature, the samples were directly imaged. The cantilever used for the measurements had a spring constant between 20-100 N/m.

4.3. RESULTS AND DISCUSSION

The physical form required of thermoplastic polymers is often coupled with subsequent processing operations to be used. Fine particles are desirable for molding and sintering compounds because smaller particles coalesce more efficiently under analogous temperature/time cycles to produce void free components. The driving force for this behavior is reduction in the large, high energy, surface area of small particles during consolidation. We are particularly interested in possibilities for preparing carbon fiber reinforced composites by applying semi-crystalline polymer powders to fiber tow, or fabric preforms, from stabilized aqueous suspensions. Carbon fibers are typically 6-8 µm in diameter. Carbon fiber reinforced structural composites are prepared with high fiber volume fractions (= 60 volume %) to take full advantage of the high stiffness and strength of these fibers. The space, at the closest point, between the fibers is calculated to be ≈ 2 µm by assuming an idealized hexagonal packing arrangement of fibers, 60 volume % fiber, and 8 µm diameter fibers. Thus, we anticipate that small particles may afford better bundle penetration, and result in more homogeneous particle distributions throughout the bundle, than larger particles.
Methods for obtaining fine particulates from semi-crystalline polymers such as PEEK by precipitation, or coagulation, are limited because the materials are essentially insoluble. Grinding operations require extensive time to achieve particles even as small as about 20 μm diameter, and are impractical for smaller particles. We previously reported a method for forming submicron diameter PEEK particles by synthesizing a soluble, ketimine containing, precursor to PEEK, then by rapidly hydrolyzing the ketimine to the corresponding ketone under acidic conditions (Figure 4-5). Conversion to the ketone could be quantitatively achieved within seconds under certain conditions, thus producing a supersaturated solution of PEEK in the N-methylpyrrrolidone solvent. Particle nucleation in the supersaturated solutions was fast; many particles formed; and sub-micron particles resulted. From a practical standpoint, we were interested in developing a method for creating supersaturated PEEK solutions without the need for first preparing a soluble polymer in a separate synthetic procedure.

The process reported in this paper (Figure 4-6) is to dissolve PEEK in a high boiling solvent at approximately the PEEK melting point. Therminol 75™, a mixture of terphenyl and quaterphenyl isomers, has a boiling point well above the PEEK melting point and is a solvent for PEEK near the polymer melting point where it cannot crystallize. The all aromatic structure of the solvent is important to maintain good thermo-oxidative stability at the elevated temperature required. The temperature of this mixture can then be rapidly quenched to yield the required supersaturated PEEK solution by pouring a colder solvent into the solution. Therminol VP-1™ was chosen as the quenching solvent because it is a liquid at room temperature (unlike Therminol
Figure 4-5. Synthesis of PEEK-ketimine precursor, and hydrolysis to PEEK
Figure 4-6. Formation of PEEK Particles in a High Temperature Solvent
and yields a miscible mixture of PEEK and the two fluids. A dark, clear PEEK solution results for an instant after quenching, then the PEEK particles rapidly precipitate. Upon particle formation, the mixture becomes quite viscous. The volume of suspension in the experiment detailed herein was ≈35 liters. Stirring was visibly inefficient after the particles formed, yet approximately 0.5-1 μm diameter particles resulted (Figures 4-7, 4-8 and 4-9). It is assumed that it is important to rapidly mix the cold solvent into the hot PEEK solution. The small particle size suggests that the stirring rate was probably not very important during the particle precipitation step (once the supersaturated solution was formed).

Analysis of the PEEK particles after formation showed that residual levels of the heat transfer fluids had become trapped in the particles. The fluids were removed by repeated extractions in THF, and gas chromatography-mass spectrometry was used to monitor the THF effluents. Diphenyl ether and o-terphenyl in the Therminol VP-1™ (T-VP1) and Therminol 75™ (T-75) respectively were the components in the heat transfer fluids present in the greatest amounts. Therefore, the decrease in heat transfer fluids in the THF extraction solvent was quantified by analysis of these two components. The peak areas of the remaining components in the heat transfer fluids decreased in a manner approximately proportional to the diphenyl ether and the o-terphenyl peak areas. The mass of Therminol VP-1™ and Therminol 75™ extracted from the PEEK were calculated for each reflux sequence using the relationships between the standards concentrations and the total ion chromatogram areas (Table 4-1). This analysis showed that almost all of the residual fluids could be removed in the first extraction.
Figure 4-7. Scanning transmission electron micrographs of particles prepared by rapidly quenching peek/therminol solutions (20,000 X mag)
Figure 4-8. Scanning transmission electron microscographs of particles prepared by rapidly quenching peek/therminol solutions (70,000 X mag)
Figure 4-9. Atomic force micrograph of a PEEK particle aggregate.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Conc. (mg/L)</th>
<th>Area (Diphenyl Ether) TIC*</th>
<th>Area (o-Terphenyl) TIC</th>
<th>mg of T-VP1/g PEEK</th>
<th>mg of T-75/g PEEK</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biphenyl-Diphenyl Ether Std.</td>
<td>0.418</td>
<td>755,366</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Terphenyl-Quaterphenyl Std.</td>
<td>0.410</td>
<td>341,901</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 1 1st extraction</td>
<td></td>
<td>1,948,535</td>
<td>1,567,665</td>
<td>23.7</td>
<td>42</td>
</tr>
<tr>
<td>Sample 2 2nd extraction</td>
<td></td>
<td>120,471</td>
<td>102,612</td>
<td>1.5</td>
<td>2.8</td>
</tr>
<tr>
<td>Sample 3 3rd extraction</td>
<td></td>
<td>1900</td>
<td>739</td>
<td>.02</td>
<td>.02</td>
</tr>
</tbody>
</table>

*Total Ion Chromatogram
The size of the PEEK particles prepared using the quenching method was analyzed using transmission electron microscopy, atomic force microscopy, and by particle size analysis with a light scattering detector. In the absence of a suspension stabilizer, these particles form aggregates in water. Aqueous suspensions were prepared by adsorbing Triton X-100™, a steric suspension stabilizer, onto the PEEK particles, then ultrasonification was used to break up the PEEK aggregates in the presence of the stabilizer. The particle size analyzer separates fractions of the particles by centrifuging fractions from the suspension, then by measuring the average particle size remaining in suspension by light scattering. Using this method, a median particle diameter of ≈0.6 μm was obtained. A drop of the suspension was placed on a substrate, and the water was evaporated. The resultant samples were analyzed by both scanning transmission electron microscopy, and atomic force microscopy (Figures 4-5, 4-6 and 4-7). The transmission electron photomicrographs show small elongated structures on the order of 1 μm long and 0.1 μm wide together with a minor amount of somewhat larger particles. A three dimensional atomic force micrograph of one of the particle structures suggests that these structures have a fibrous nature (Figure 4-7). This fibrous structure is typical of semi-crystalline polymers where precipitation from solution is promoted by a crystallization process. The oblong nature of the particles is presumed to be a result of the shear force imposed by stirring on the crystallization process.

Thermal analysis of the particles prepared by rapid quenching demonstrates that the percentage of crystallinity, as well as the transitions, are similar to the PEEK powder which was originally used in preparing the particles (Table 4-2). The samples described in Table 4-2 are the PEEK as received.
Table 4-2. Thermal Properties of PEEK before and after particle formation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_g^\circ C$</th>
<th>$T_m^\circ C$</th>
<th>$\Delta H_f$ J/gram</th>
<th>% Cryst$^1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Victrex PEEK 450PF™</td>
<td>150-151</td>
<td>340</td>
<td>43</td>
<td>33</td>
</tr>
<tr>
<td>PEEK particles before extraction</td>
<td>146-147</td>
<td>341</td>
<td>39</td>
<td>30</td>
</tr>
<tr>
<td>Purified PEEK particles</td>
<td>149-150</td>
<td>339</td>
<td>41</td>
<td>32</td>
</tr>
</tbody>
</table>

1. Based on $\Delta H_f = 130$ J/gram for 100% crystalline PEEK.
from Victrex (prior to particle preparation), the PEEK particles which contained residual amounts of the heat transfer fluids (prior to the extractions described in Table 4-1), and the purified particles. The level of crystallinity in the PEEK particles was calculated based on an enthalpy of fusion representing 100% crystallinity of 130 J/g $^{10}$. Calculations from the gas chromatography-mass spectrometry analyses showed that the second entry in Table 2 contained approximately 6.5 wt. percent of residual heat transfer fluids. These impurities reduced the glass transition temperature by approximately 3-4°C, and resulted in slightly reduced crystallinity. The thermal properties of the purified PEEK particles were quite similar to the original material.

4.4. CONCLUSIONS

Fine, semi-crystalline poly(ether ether ketone) particles can be prepared by forming highly supersaturated solutions of these materials. These supersaturated solutions can be formed by rapidly quenching the solutions by adding a cold solvent, or by chemically transforming a soluble material to the semi-crystalline polymer isothermally. Rapid quenching is desirable in that it eliminates the necessity for a separate synthesis process in preparing a soluble precursor. The aromatic heat transfer fluids used for a solvent in this process appear to be good solvents for several commercial semi-crystalline poly(arylene ether)s and poly(arylene sulfide)s. Notably, a similar process was successfully demonstrated on about a one liter scale with poly(phenylene sulfide) (Phillips Petroleum) and with the poly(ether ketone) prepared from a mixture of terephthaloyl and isophthaloyl chlorides and diphenyl ether (DuPont’s PEK material). Future work will focus on developing aqueous suspensions of these materials for composite fabrication.
ACKNOWLEDGMENTS

I would like to thank Monsanto Chemicals for the generous donation of Therminol VP-1. This research was supported by the NSF Science & Technology Center for High Performance Polymeric Adhesives and Composites at VPI & SU.

4.5. REFERENCES


(9) Texier, A.; Davis, R. M.; Lyon, K. R.; A.Gungor; McGrath, J. E.; Marand, H.; Riffle, J. S. *Polymer* 1993, 34, 896-906.

Chapter 5. Epoxy and Hydroxy Functional Polyolefin Macromonomers

5.1. SYNOPSIS

In this chapter, the methods that have been developed for preparing saturated polyolefin oligomers with Si-H, epoxy groups, and with dihydroxy groups will be reported. Anionic polymerization of butadiene, then termination of the chains with chlorodimethylsilane leads to controlled molecular weight oligomers with silane functionality, and wherein the microstructure can be tailored. Hydrogenation of these materials proceeds smoothly using colloidal nickel catalysts to yield the corresponding saturated materials, which are stable to conditions used for melt polyesterifications. Hydrosilation of allyl glycidyl ether with the Si-H endgroups produces epoxy functional oligomers, and subsequent hydrolysis of the epoxy rings yields oligomers with a dihydroxy group at one end. Melt copolymerization of the olefin macromers with 1,4-butandiol and 1,4-dimethylcyclohexanedicarboxylate in the presence of titanium isopropoxide affords poly(ester-g-olefin) graft copolymers. These copolymers are under study as model interfacial agents for polyester/polyolefin blends and as suspension agents for polyester particles in non-polar media.

5.2. INTRODUCTION

Major interest exists in the development of mechanically compatible melt blends of polyesters with polyolefins. Polyolefins form the largest group of commercial thermoplastics. Over 34 billion pounds of thermoplastic polyolefins were produced in 1995 alone. They have excellent moisture resistance, excellent processibility, and generally, low glass transition temperatures, but are generally susceptible to attack by hydrocarbon solvents. In contrast, the
relatively polar, semi-crystalline commodity polyesters, (primarily poly(ethylene terephthalate) and poly(butylene terephthalate)) have higher strengths and melting points, but are more moisture sensitive than the commodity polyolefins. Blending polyesters with polyolefins can provide a method of producing materials with intermediate properties to the homopolymer materials. In this way, a specialized blend of polymers may be formulated for a given application, with better performance than the lower cost component, and lower price than the higher cost component. For example, a polyester-polyolefin blend could show decreased moisture sensitivity and improved impact resistance compared to the polyester component and higher strength, and improved fuel resistance compared to the polyolefin component. Another potential benefit is in the ability to control gas permeability by changing the blend composition.

From a practical viewpoint however, blends of polar polyesters with non-polar polyolefins with desirable mechanical and physical properties are not likely to be obtained via direct blending of a polyester with a polyolefin. As discussed in the next section, polymer blends which are homogeneous on a molecular level, or thermodynamically miscible are few and far between because of unfavorable specific interactions and negligible entropies of mixing.

5.2.1 Thermodynamic Miscibility of Blends

Thermodynamically miscible blends result when the free energy of mixing two polymers ($\Delta G_m$) is negative. The Flory-Huggins theory uses a lattice representation for a polymer solution or blend to calculate the entropy change upon mixing one long chain molecule and a solvent, or two long chain molecules. (Newer theories that have added additional elements to the Flory-Huggins model more closely match empirical data with their treatment, but the
Flory-Huggins model is sufficient for discussing basic concepts). The free energy of mixing for two polymers can be given by the Flory-Huggins model by the following expression:

\[ \Delta G_m = RTV \left[ \chi_{AB} \phi_A (1 - \phi_A) + \left( \phi_A \rho_A / M_A \right) \ln \phi_A \right] + \left( \phi_B \rho_B / M_B \right) \ln \phi_B \]

The important parameters in establishing miscibility of the two polymers are the molecular weights of the polymers being blended \((M_A \text{ and } M_B)\), and the interaction parameter \((\chi_{AB})\) which is a measure of the enthalpy of mixing for the polymers being blended. For the components to be thermodynamically miscible, the free energy of mixing \((\Delta G_m)\) should be negative. As the molecular weights of the polymers increase, the magnitude of the negative entropic contribution to \(\Delta G_m\) decreases. It is necessary to have negative enthalpies (quantified by \(\chi_{AB}\)) of mixing between the polymer components being blended to maintain a negative \(\Delta G_m\). This usually only results when strong specific interactions exist between the blended components through mechanisms such as hydrogen bonding, but can also exist when the chemical compositions and the solubility parameters of the polymer components are very similar. Most polymer blends are not thermodynamically miscible, and separate into discrete phases upon blending. These phase morphologies are dependent upon composition, and may be composed of polymer lamellae or layers, discrete spheres of one polymer in a continuous matrix of the other, polymer rods, or two intertwining co-continuous matrices. Typically, for immiscible polymer blends, the weak link in the mechanical properties of the blend occurs at the weak interface between phases.
5.2.2 Compatibilized Blends

Forming blends of polyolefins with polyesters is intrinsically difficult due to their widely different solubility parameters. Thermodynamically miscible one-phase blends of polar polyesters with non-polar polyolefins is generally not possible. However, to achieve desirable properties for commercial applications, thermodynamic miscibility is not necessary. Compatibilized blends, refers to blends where one component is dispersed in a second component, and there is good interfacial adhesion between phases. Dispersions of immiscible components may be achieved by reducing the surface energy at the phase interface. Dispersion of phases in immiscible polymer blends may be achieved by use of a relatively low molecular weight surfactant, however to also achieve adequate mechanical properties, polymeric surfactants are needed, as the high molecular weight blocks will result in entanglements reaching from one immiscible phase to the second, thus providing mechanical strength at the junction between the immiscible phases. For a binary immiscible polymer blend, the polymeric surfactant may have several designs, including di-block copolymers, and graft copolymers.

5.2.3 Graft Copolymers as Blend Compatibilizers

Graft copolymers are key to achieving desirable properties in several classes of industrial polymeric blends. Greber, then Milkovich and Schultz and Milkovich, pioneered the use of suitably functionalized macromonomers for preparing such copolymer architectures. Since that time, these materials have generated widespread industrial interest as blend compatibilizers and as laminate adhesives for combining commodity polymers.
such as polyesters with polyolefins. This chapter describes the preparation of saturated polyolefin macromonomers with one dihydroxy functional endgroup and one nonfunctional end. Initial results show that these can be incorporated as grafts into polyester backbones using melt, step-growth reactions to afford poly(ester-g-olefin) graft copolymers\textsuperscript{6}. Epoxy functional oligomers serve as precursors for the dihydroxy functional macromonomers\textsuperscript{7,8}.

Anionic polymerizations of 1,3-dienes with narrow molecular weight distributions are well documented\textsuperscript{9}. The effects of solvents, counterions, and the nature of additives on the microstructures obtained have been studied and many of these effects are well understood\textsuperscript{10-13}. The living anions of these polymers have been precisely functionalized with a variety of structures including hydroxy\textsuperscript{14}, amino\textsuperscript{15}, and carboxyl groups (in the case of styryl anions)\textsuperscript{16,17}. Chlorosilanes have been used as terminating reagents to make both star\textsuperscript{18} and linear polymers\textsuperscript{19,20}. Previous research on epoxy functional polydienes\textsuperscript{21,22} includes terminating living anions with silanes containing combinations of epoxy and alkoxy groups and also direct reaction of epichlorohydrin with aluminum alkylate functional endgroups. In this research project, epoxy functional, saturated, polyolefin oligomers have been prepared by first terminating the living polymerization of 1,3-dienes with chlorodimethylsilane; subsequently saturating the double bonds; then by hydrosilating allyl glycidyl ether with the silicon hydride endgroups. The resultant epoxy groups were hydrolyzed in the presence of an organic acid catalyst to yield the desired dihydroxy functional endgroups.
5.3. EXPERIMENTAL

5.3.1 Materials

Cyclohexane was obtained from Aldrich and stirred over concentrated sulfuric acid for a week, then passed through a column containing basic alumina and molecular sieves. It was passed through a similarly packed column again and distilled just prior to use. Sec-butyl lithium in cyclohexane, kindly supplied by Lithco Corp., was titrated with 2,5-dimethoxybenzyl alcohol. Tetrahydrofuran was refluxed over sodium under a blanket of argon using benzophenone as an indicator; then distilled just prior to use. Butadiene was kindly supplied by Phillips Petroleum Co., and was passed through a column of basic alumina and molecular sieves prior to use. Chlorodimethylsilane was degassed and distilled over CaH₂. Nickel octoate was obtained from Shepherd Chemical Co. and the crude material was extracted with cyclohexane. After evaporating the solvent and drying the nickel octoate in a vacuum oven at 100°C for 2 days, a solution of known concentration was prepared in dry cyclohexane and stored under a positive pressure of nitrogen. Triisobutylaluminum, chloroplatinic acid, triflic acid, titanium (IV) isopropoxide, and allyl glycidyl ether were obtained from Aldrich Chemicals. Allyl glycidyl ether was distilled over CaH₂ and stored in brown bottles under a positive pressure of nitrogen.

1,4-Dimethylcyclohexanedicarboxylate was prepared by esterification of the corresponding acid with methanol using p-toluenesulfonic acid as the catalyst. 1,4-Butanediol, obtained from Kodak chemicals, was dried over CaH₂ and distilled under vacuum, then stored in a septum sealed bottle until used. 1,3,5-
Trimethyl-2,4,6-tris(3,5-ditertbutyl-4-hydroxybenzyl)benzene (Ethanol 330 stabilizer) was obtained from Ethyl Corporation.

5.3.2 General Procedures for the Preparation of Si-H Terminated Poly(butadiene)s

The following procedure is for a silane terminated poly(butadiene) macromer with \( <M_n> = 280 \text{ g/mol}, \approx 5 \) repeat units per graft. All of the poly(butadiene) oligomers discussed herein were prepared using a similar procedure. A pressure bottle containing a stir bar was sealed with a stopper and flame dried under a slow stream of nitrogen. THF (freshly distilled over sodium, \( \approx 25 \times \text{moles sec-BuLi} \)), followed by 80 mL dry cyclohexane, were transferred to the pressure bottle via a cannula under a positive pressure of nitrogen. It should be noted that 25 moles THF per mole initiator were used in this reaction. The very low targeted molecular weight required significantly more initiator than the remainder of the oligomer series. For the remainder of the oligomers described in Table 1, 50 moles THF per mole initiator were used to increase the percentage of 1,2-microstructure obtained. A dry stainless steel container fitted with a needle attached to a valve was conditioned with sec-BuLi and washed with cyclohexane; then charged with butadiene and weighed. The butadiene was transferred to the pressure bottle containing the THF/cyclohexane mixture via the needle on the container, then the stainless steel container was reweighed to calculate the amount of butadiene charged (in this case, 34 g). The pressure bottle was cooled in a dry ice/isopropanol bath. Sec-butyl lithium (1.28 M in cyclohexane, 95 mL, 0.1216 mole, Mn of polybutadiene \( \approx 280 \text{ g/mole} \)) was transferred into another stainless steel
container (also previously treated with sec-butyl lithium and washed with cyclohexane) fitted with an addition needle; then the container was pressurized to 60 psi with nitrogen. The needle was inserted into the pressure bottle and sec-BuLi was forced into the flask. The reaction mixture immediately turns a strong yellow color indicating rapid formation of the butadiene anion. The pressure bottle was kept in the dry ice/isopropanol bath for 5 minutes to control the exotherm, then the bath was removed and the reaction was allowed to come to room temperature while stirring over a period of 35 minutes. Meanwhile, chlorodimethylsilane was distilled over CaH₂. The reaction was terminated by adding chlorodimethylsilane (20.3 mL; 0.183 mole) via syringe at room temperature. The yellow color characteristic of the anion immediately disappeared and LiCl precipitated. The mixture was stirred at room temperature overnight and filtered to remove LiCl. The solvent was removed; the oligomer was dissolved in hexane, filtered again, and concentrated. The oligomer was dried at 60°C under 500 mtorr vacuum. This procedure yielded a polybutadiene oligomer with 58% 1,2-microstructure. For the remainder of the series, 70-90% 1,2-microstructure resulted, presumably because of the higher ratio of THF/initiator employed in those reactions.

5.3.3 General Procedures for Hydrogenation of Si-H Terminated Poly(butadiene) Oligomers

The Si-H terminated poly(butadiene) described above (34 g., 0.8 mole of double bonds) was dissolved in 300 mL dry cyclohexane and transferred to a Parr pressure vessel under nitrogen. A 7.1 mL aliquot of nickel octoate solution (0.08 g/mL nickel octoate in dry cyclohexane), which corresponds to 0.2 mole %
Ni based on total double bonds, was charged to a separate dry bottle and a solution of triisobutylaluminum (4.8 mL, 1M solution in toluene, 3 moles of Al per mole of Ni) was added. The colloidal Ni obtained was aged at room temperature for 15 minutes and added to the reactor using a syringe. The nitrogen in the reactor was replaced with 50 psi hydrogen, the reactor was heated to 65-70°C with agitation, and the 50 psi H₂ pressure was maintained. Reaction progress was monitored using ¹H NMR by observing the disappearance of the olefinic peaks from 4.8-6.0 ppm. Upon completion, the contents of the reactor were cooled to room temperature. The reaction mixture was treated with a 5% solution of tartaric acid until the brown color of the catalyst disappeared. The organic layer was separated and the oligomer was isolated by removing the solvent. The oligomer was dried under vacuum at 500 mtorr and 80°C for 12 hrs. The structure of these saturated polyolefin oligomers depends on the microstructure of the precursor polybutadienes. The polar media used for the anionic polymerizations yields predominantly 1,2-polybutadiene microstructure, which results in polyolefin oligomers high in poly(1-butene) content after hydrogenation.

### 5.3.4 General Procedures for Preparing Epoxy terminated, Saturated Polyolefin Oligomers

A dry, two necked flask was charged with 85 mL of a 1:1 v/v mixture of THF and allyl glycidyl ether under nitrogen. An addition funnel was charged with a solution of 34 g of the Si-H terminated polyolefin in another 85 mL of the 1:1 v/v mixture of THF and allyl glycidyl ether; then fitted to the reaction flask. The reactants were kept under a slow purge of nitrogen. A solution of
chloroplatinic acid (118 mg in 10 mL of allyl glycidyl ether) was added to the mixture of allyl glycidyl ether and THF in the flask and stirred for about an hour. The oligomer solution was added in aliquots of \( \approx 20 \) mL at room temperature and reaction progress was followed by IR spectroscopy. Each aliquot was added after the disappearance of the Si-H peak at 2116 cm\(^{-1}\). After addition was complete, the reaction mixture was stirred at room temperature overnight, then allyl glycidyl ether and THF was removed by heating under reduced pressure. In order to remove residual amounts of allyl glycidyl ether, toluene was added to the mixture and evaporated in a rotary evaporator several times. During solvent evaporation, the reaction mixture turns brown due to thermal decomposition of platinum salts. The decomposed platinum salts were removed in the following manner. A column was packed with Celite and activated charcoal and washed with chloroform. The oligomer was dissolved in chloroform and eluted slowly through the columns. A yellow solution of oligomer was obtained which was concentrated and dried under vacuum at 200 mtorr and 80-85°C for 12 hrs. Quantitative hydrosilation was confirmed using proton NMR and non-aqueous epoxy group titrations. To titrate the epoxy groups, the sample was dissolved in chloroform and an excess of tetrabutylammonium bromide in glacial acetic acid was added to produce a homogeneous solution. Aliquots were titrated with a standardized solution of perchloric acid in glacial acetic acid. The tetrabutyl- ammonium bromide functions as a phase transfer catalyst by reacting with the perchloric acid titrant to produce HBr in situ. Epoxy groups are thus titrated with HBr in glacial acetic acid. The molecular weight of the epoxy terminated polyolefin from this reaction
was approximately 400 g/mol, which is the molecular weight of the silane
terminated oligomer (280 g/mol) plus the new endgroup.

5.3.5 General Procedures for Preparing Dihydroxy Terminated
Saturated Polyolefin Oligomers

The epoxy terminated polyolefin oligomer (37.5 g, ≈ 400 g/mol, 0.094
mole) was dissolved in 228 mL THF (2.8 moles, =30 x moles epoxy groups).
Water (1.41 moles, =15 x moles epoxy groups, 25.4 mL), followed by 1.76 g
triflic acid (0.13 mole per epoxy group, 0.01175 mole) was added to that
solution, and the mixture was stirred at room temperature. Reaction progress
was followed by $^1$H NMR by monitoring the disappearance of peaks at 2.6-3.7
ppm corresponding to the epoxy groups. After all the epoxy groups were
consumed, the reaction mixture was diluted with chloroform and washed with a
saturated solution of bicarbonate followed by brine solution. The organic layer
was dried over anhydrous K$_2$CO$_3$, filtered and concentrated to yield the
dihydroxy terminated polyolefin. The oligomer was dried under vacuum at 200
mtorr and 90°C for 12 hrs.

5.3.6 General Procedures for Preparing Poly(ester-g-olefin)
Copolymers.

A pressure vessel was charged with 11.5 g (0.0288 mole) of the
dihydroxy functional polyolefin and 2.88 g (0.0144 mole) of 1,4-
dimethylcyclohexanedicarboxylate. Titanium isopropoxide was added (0.001
mole per mole of ester, 0.51 mL from a stock solution of 0.16 g in 20 mL toluene,
1.44 x 10^{-5} mole, 4.09 x 10^{-3} g) followed by Ethanox 330 stabilizer (0.1 wt. % of
oligomer, 0.0115 g) and the reaction was heated at 200-210°C for 20 hrs. with a slow stream of N₂ passing through the mixture. After 20 hours, ¹H NMR indicated that the reaction was essentially complete since only a residual amount of methoxy groups (at 3.65 ppm) remained. The resultant material was used for the copolymerization described in the next step. The transesterified "macroester" (7.0 g, 0.0175 mole) was transferred to a reactor fitted with a stirrer and a distillation apparatus. 1,4-Dimethylcyclohexanedicarboxylate (10.5 g, 0.0525 mole, 6 moles per "macroester") and 1,4-butanediol (9.46 g, 0.105 mole) were added. The reaction mixture was heated to 200-210°C for 2 hours with a slow stream of nitrogen flowing through the flask to assist the removal of methanol. The distilled methanol was collected (2.9 g, 89% of the theoretical amount); then the temperature was increased to 230-240°C and a vacuum was applied for an additional 2.5 hours. During this period, 4.2 g butanediol (89% of the theoretical amount) distilled from the reaction into the collection flask. The reaction was stopped by cooling and releasing the vacuum. The crude reaction product was a grey solid. It was dissolved in chloroform, precipitated into methanol, filtered, and suspended in hexanes. The slurry was stirred and filtered, and the filtered sample was dried under vacuum at room temperature.

5.3.7 Characterization

GPC chromatograms for the graft copolymers (including all chromatograms in Figure 5-7) were obtained on a Waters Model 590 instrument fitted with 10⁴ and 10³ Å µ Styragel columns using chloroform as the eluent, and calibrated against polystyrene molecular weight standards using a
refractive index detector. The absolute molecular weights for the oligomers (detailed in Table 5-1) were determined using a Waters Model 150C GPC instrument with differential viscosity and refractive index dual detectors and universal calibration of 4 x (300 x 7.8 mm i.d.) steel columns packed with 10-mm Permagel. 1H NMR was conducted in deuterated chloroform using a Varian Unity 400 Spectrometer operating at 400 MHz. Fourier transform IR spectroscopy was conducted on a Nicolet Impact 400 Instrument.

5.4. RESULTS AND DISCUSSION

Our objective was to prepare graft copolymers comprised of polyester backbones with polyolefin grafts to use for compatibilizing polypropylene with polyesters, and also to stabilize dispersions of polyester particles in hydrocarbon oils. The methodology was to prepare a saturated polyolefin graft having a high atactic poly(1-butene) composition to afford an amorphous material where the solubility parameter of the graft approximated that of poly(propylene). Thus, butadiene was polymerized in polar media using well known anionic reactions, then subsequently hydrogenated. New functionalization methods generated a diol at one chain end. Then the "macrodial" was copolymerized with butanediol and diester monomers in melt polymerizations to prepare poly(ester-g-olefin) copolymers.

Butadiene was initiated with sec-butyl lithium and polymerized in a mixture of cyclohexane and 25-50 moles tetrahydrofuran per mole of initiator under living anionic conditions to prepare the oligomeric precursors to the copolymer grafts (Figure 5-1)\(^6\). The polar solvent mixture promoted formation of \(\approx 60-90\%\) of the desired atactic 1,2-microstructure in the oligomeric materials,
Figure 5-1. Preparation of Epoxy Terminated Polyolefin Macromers
which, upon hydrogenation, yielded polymers high in poly(1-butene) content. These living anions were terminated with chlorodimethylsilane to form polybutadiene chains with a non-functional hydrocarbon tail and a silicon hydride at the chain head. Cyclohexane with added dipiperidinoethane was also explored as a polymerization medium for these silane functionalized oligomers. As expected, those polymerizations yielded oligomers with ≈ 95% of the 1,2-microstructural content, higher than that obtained with the THF/cyclohexane mixture. Unfortunately, when chlorodimethylsilane was added to the polymerizations containing dipiperidinoethane, an immediate gelatinous white precipitate appeared, believed to be due to complexation between the chlorosilane and tertiary amine. Since this mixture proved difficult to purify, THF/cyclohexane was used for subsequent reactions.

Both microstructure and $M_n$ of the polymers were determined by $^1$H NMR (Figure 5-2). Number average molecular weights calculated by comparing the areas under the peaks corresponding to the endgroups (in this case two methyl groups on the silicon) relative to the olefinic protons in the chain correlated well with those obtained by GPC using a universal calibration technique (Table 5-1). The microstructure content was calculated by comparing areas under the methylene olefinic peaks in the pendant vinyl group (peak "d" in Figure 5-2) to the methine olefin peaks (peaks "e" in Figure 5-2). Infrared spectra of the oligomers also qualitatively confirm the silane endgroup structure by exhibiting a strong absorbance at 2116 cm$^{-1}$, characteristic of Si-H stretching.

Colloidal nickel is among the several reduction catalysts that readily hydrogenate polydiienes to the corresponding saturated polyolefins. The colloidal nickel catalyst used for this work was prepared by pre-reacting a
Figure 5-2. $^1$H NMR of Si-H Terminated Poly(butadiene) used for Determining both Molecular Weight and Polydiene Microstructure.
Table 5-1. Molecular Weight and Microstructure of Si-H Functional Poly(butadiene) Oligomers

<table>
<thead>
<tr>
<th>$&lt;M_n&gt;$ (GPC)*</th>
<th>Polydispersity</th>
<th>$&lt;M_n&gt;$ (NMR)</th>
<th>$&lt;M_n&gt;$ (VPO)</th>
<th>% 1,2-Microstructure</th>
</tr>
</thead>
<tbody>
<tr>
<td>6570 g/mol</td>
<td>1.12</td>
<td>5400 g/mol</td>
<td>5080 g/mol</td>
<td>89.2</td>
</tr>
<tr>
<td>2980 g/mol</td>
<td>1.02</td>
<td>2300 g/mol</td>
<td>2253 g/mol</td>
<td>83.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>440 g/mol</td>
<td></td>
<td>73.2</td>
</tr>
</tbody>
</table>

*Universal Calibration
hydrocarbon solution of nickel octoate (a hydrocarbon soluble nickel salt) with a trialkylaluminum. Reduction of the silane functional polybutadiene oligomers with hydrogen in the presence of this catalyst proceeded smoothly to produce saturated products with only trace amounts of olefin remaining. It is believed that the residual double bonds after hydrogenation may be due to trace amounts of trans-1,4-microstructure in the oligomers, which should be difficult to reduce. One should recognize that double bonds remaining in the graft materials were of particular concern since these would lead to oxidatively labile allylic sites. In the absence of antioxidants, the high temperature melt polyesterrification conditions used to form the graft copolymers caused gel formation, probably due to crosslinking through the residual double bonds present in the polyolefin. The addition of antioxidants prior to the copolymerizations eliminated this problem.

Nickel salts have also been used as catalysts for hydrosilation reactions\textsuperscript{24}. Thus, it was important to establish the quantitative retention of Si-H endgroups after hydrogenation. The area under the peaks of the methyl groups bonded to silicon (0 ppm) and the hydrogen on silicon (3.85 pm) prior, and subsequent, to hydrogenation remained unchanged in the proton NMR spectra (Figure 5-3), indicating that the endgroups remained intact. An alternate order of reactions, i.e., direct hydrosilation of allyl glycidyl ether with the silane functional polydiene, then hydrogenation, was also investigated as a potential route to the desired epoxy functional materials. However, this route was abandoned because proton NMR indicated loss of a portion of the epoxy endgroups during the hydrogenation process.
Figure 5-3. Hydrogenation of Si-H Terminated Polydiene to Polyolefin
The epoxy group was introduced at the chain ends by hydrosilating allyl glycidyl ether with the silane terminated oligomer in the presence of chloroplatinic acid. An advantage of using this reaction sequence for preparing functionalized polyolefin macromers is that it offers versatility of functional groups at the hydrosilation stage. For example, it should be possible to use the Si-H endgroup to hydrosilate a variety of allylic molecules containing groups such as epoxy, cyano, ester, keto, etc. A 1:1 mixture of THF and allyl glycidyl ether was used as the hydrosilation medium in this case since the hydrocarbon macromer was not soluble in allyl glycidyl ether alone, and reaction progress was easily monitored by the disappearance of the Si-H stretch in the infrared spectrum. Following hydrosilation, the mixture was heated under vacuum to remove excess allyl glycidyl ether, and to decompose the platinum catalyst; then the decomposed platinum was removed by passing a solution of the polymer through a column of activated charcoal. $^1$H NMR of the epoxy functionalized polyolefin (Figure 5-4) as well as titration of the epoxy groups with hydrobromic acid established quantitative hydrosilation.

Epoxy endgroups on the macromonomers were ring opened to diol endgroups using an acid catalyzed nucleophilic reaction of small amounts of water dissolved in THF (Figure 5-5). The reaction is complicated by the non-polar nature of the macromonomer substrates reacting with the highly polar water molecules. Table 5-2 summarizes representative results. The failure of entry 1 in the table suggests that interfacial reactions are not efficient. Interestingly, epoxy ring opening on the hydrophobic polymer is also sensitive to the amount of water present in systems which visibly appear to be homogeneous. Although the reaction exemplified in entry 2 appeared clear
Figure 5-4. $^1$H NMR of Epoxy Terminated and Dihydroxy Terminated Polyolefins
Figure 5-5. Preparation of Dihydroxy Functional Polyolefin Macromers
<table>
<thead>
<tr>
<th>Polymer Mn</th>
<th>[THF] [Polymer]</th>
<th>[H₂O] [Polymer]</th>
<th>[TfOH] [Polymer]</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>500 g/mol</td>
<td>---</td>
<td>H₂O as Solvent</td>
<td>8</td>
<td>No Reaction</td>
</tr>
<tr>
<td>3000 g/mol</td>
<td>350</td>
<td>800</td>
<td>0.2</td>
<td>No Reaction</td>
</tr>
</tbody>
</table>
| 5000 g/mol | 1000            | 100             | 3.5             | (a) Quantitative Reaction  
            |                 |                 |                 | (b) Bimodal MW Distribution  
            |                 |                 |                 | (c) THF Cleavage |
| 400 g/mol  | 30              | 15              | 0.125           | (a) Quantitative Reaction  
            |                 |                 |                 | (b) Unimodal MW Distribution  
            |                 |                 |                 | (c) THF Cleavage |
and homogeneous throughout the process, the relatively high concentrations of water hindered reaction progress. It is believed that this "sluggish" reactivity may be caused by micellar, or aggregated, polymer solutions. By contrast, substantially decreasing the water content yields quantitative ring opening (see entries 3 and 4 in Table 5-2). NMR spectroscopy confirmed conversion of the epoxy functional oligomers to the diol functional materials (Figure 5-5). It is also important that very low acid concentrations relative to water be used for these reactions in order to obtain quantitative epoxide opening without chain extension. Chain extension can be easily recognized in the GPC chromatograms since addition of each successive macromonomer to a chain results in a significant build-up of molecular weight, and therefore yields bimodal chromatograms (contrast entries 3 and 4 in Table 5-2). It should also be noted that low levels of butanediol formed from ring opening the THF solvent could be detected by NMR at elevated triflic acid concentrations.

One synthetic problem in copolymerizing polyolefins with diester and diol monomers normally used for polyester homopolymers is the polarity difference between the reacting species, especially since solvent free reactions are desirable. Reaction conditions for graft copolymerization were established using the lowest molecular weight dihydroxy terminated oligomer in the series (400 g/mole) and 1,4-dimethylcyclohexanedicarboxylate, an aliphatic diester, to minimize a possible compatibility mismatch. Under these conditions, the copolymerization exhibited a transparent melt throughout the reaction, suggesting phase miscibility. A careful investigation of oligomeric molecular weight with respect to the homogeneity of these reactions, as well as a study of
analogous reactions using aromatic diesters, is recommended to establish possible limits on compositions.

A one-pot, three step reaction sequence was employed to pre-react a significant amount of the macromonomer with the diester, for the purpose of efficiently incorporating the macromonomer into the copolymer (Figure 5-6). First, two moles of the dihydroxy functional macromonomer were used to partially "cap" one mole of the dicarboxylate via transesterification in the presence of titanium isopropanoxide at 200-210°C. Since the macrodial contains one primary and one secondary hydroxyl group, one might expect the more reactive primary hydroxyl group to react preferentially at this stage. Quantitative reaction was established by noting the disappearance of the methoxy groups from the diester using proton NMR, and also by measuring the quantitative evolution of methanol distilled from the flask. GPC demonstrates an expected increase in molecular weight following this first step (Figure 5-7, chromatogram B). However, a substantial amount of unreacted macromonomer also remains after this step (Figure 5-7, peak B1), and some chain extension has taken place (Figure 5-7, peak B2). Statistical calculations for the mole and weight percentages of unreacted macromonomer assuming equal reactivity of hydroxyl groups, two moles macromonomer to one mole of the diester, and quantitative reaction predict that 50 mole percent and 22 weight percent should remain (see Appendix 1 for calculations). By contrast, if the primary hydroxyl group had reacted in complete preference to the secondary group, no unreacted macromonomer should remain. The relative areas of the two peaks on the GPC chromatogram (Figure 5-7, chromatogram B) corresponding to the macromonomer and to the esterified species were deconvoluted, and their
Figure 5-6. Poly(ester-g-olefin) Copolymerization
A: Dihydroxy functional polyolefin

B: $B_1$ is dihydroxy functional polyolefin remaining
$B_2$ is the "capped" ester

C: Copolymer

![Graph showing elution volume with peaks A, B1, B2, C]

<table>
<thead>
<tr>
<th>peak</th>
<th>Mn</th>
<th>MWD*</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>600</td>
<td>1.05</td>
</tr>
<tr>
<td>$B_1$</td>
<td>600</td>
<td>1.02</td>
</tr>
<tr>
<td>$B_2$</td>
<td>1600</td>
<td>1.65</td>
</tr>
<tr>
<td>C</td>
<td>8200</td>
<td>3.00</td>
</tr>
</tbody>
</table>

*Polydispersity Index
**Calibrated against polystyrene stds.

Figure 5-7 Poly(ester-g-olefin) Copolymer Formation Characterized by GPC

224
relative areas were assessed (16% and 84% respectively). Since a refractive
index detector was used for the chromatogram, one cannot expect the peak
areas to strictly correlate with the weight percentages of polymer. However, the
relatively large macromonomer peak area does suggest that the primary
hydroxyl group did not react in substantial preference to the more sterically
hindered secondary hydroxyl group under the particular conditions employed
for this reaction.

In the second stage of these reactions, sufficient 1,4-
dimethylcyclohexanedicarboxylate and an excess of 1,4-butanediol were
added to the mixture to provide the desired polyester-polyolefin weight
composition. The remainder of the polyesterification reaction steps were
conducted in a conventional manner for polymerization of diesters with aliphatic
alcohols.26 No additional transesterification catalyst was added after the first
step. Transesterification of 1,4-dimethylcyclohexanedicarboxylate with
butanediol begins at \( \approx 200^\circ C \) while methanol is distilled, then the reaction
mixture is allowed to undergo polycondensation at 230-240°C under vacuum.
During the latter stage, the butanediol by-product was vacuum distilled forcing
the buildup of molecular weight (Figure 5-7). GPC traces suggest incorporation
of the macromonomer under these conditions.

5.5. CONCLUSIONS

Methods for preparing both epoxy and dihydroxy functional, saturated,
olefin macromonomers with controlled graft lengths have been defined.
Feasibility results using the diol macromers to prepare poly(ester-g-olefin)
copolymers in melt copolymerizations indicate formation of the desired
materials. The effects of graft length, graft copolymer composition, and diester structure on phase homogeneity during copolymerization will be the focus of continuing work. The utility of these materials as blend compatibilizers and as dispersion stabilizers for polyesters in hydrocarbon media will follow.

5.6. ACKNOWLEDGEMENTS

Thanks to Eastman Chemical Co. for their financial support and technical discussions. Thanks to Phillips Petroleum for the generous supply of butadiene.

5.7. REFERENCES

5.8. Appendix

Statistical calculations for the mole percentages and weight percentages of x-mers in the reaction product of two moles 400 g/mole dihydroxy functional macromonomer with one mole of 1,4-dimethylcyclohexanedicarboxylate (the first stage of the reaction in Scheme 3) are provided. The calculations are based on two assumptions: (1) The reaction is quantitative (i.e., no even numbered x-mers occur), and (2) The probability of any hydroxyl group reacting is equal.

Let \( p \) equal the probability that a hydroxyl group has reacted \((p = 0.5)\). Let \((1-p)\) equal the probability that a hydroxyl group has not reacted \((1-p = 0.5)\). Then the probability of unreacted macromonomer (1-mer) occurring is \((1-p)^2\). The probability of a 3-mer occurring is \((1-p)^2p^1\). The probability of a 5-mer occurring is \((1-p)^2p^2\).

3-mer:

\[
\text{HO} \quad \text{O-C-R-C-O} \quad \text{OH}
\]

5-mer:

\[
\text{HO} \quad \text{O-C-R-C-O} \quad \text{O-C-R-C-O} \quad \text{OH}
\]

The probability distribution function on a mole fraction basis is thus:
\[
\frac{P(n)}{\sum P(n)} = \frac{(1-p)^2 p^n}{\sum (1-p)^2 p^n}
\]

where \( n = 0 \) for unreacted macromonomer, \( n = 1 \) for a 3-mer, \( n = 2 \) for a 5-mer, etc.

\[
\frac{(1-p)^2 p^n}{\sum (1-p)^2 p^n} = \frac{(1-p)^2 p^n}{(1-p)^2 \sum p^n} = \frac{(1-p)^2 p^n}{(1-p)^2 \frac{1}{1-p}} = \frac{(1-p)^2 p^n}{1-p}
\]

The mole fraction of macromonomer which should remain under these constraints is

\[
\frac{(1-p)^2 p^0}{1-p} = \frac{(0.5)^2}{0.5} = 0.5
\]

Likewise, the mole fraction of 3-mer which should occur is

\[
\frac{(1-p)^2 p^1}{1-p} = \frac{(0.5)^2 \cdot (0.5)}{0.5} = 0.25
\]

Each of the mole fractions can be converted to a weight fraction by multiplying the mole fraction by the weight of the respective x-mer, then by dividing the product by the sum of the weights, e.g.

\[
\text{weight fraction x-mer} = \frac{(\text{mole fraction x-mer}) \times (\text{MW of x-mer})}{\sum (\text{mole fractions x-mers}) \times (\text{MW of x-mer})}
\]
Table 5-3. Probability Distributions For Reaction Of 2 Moles
Macromonomer With 1 Mole Diester

<table>
<thead>
<tr>
<th>x-mer</th>
<th>mole fraction x-mer</th>
<th>(mole fraction x-mer) (MW x-mer)</th>
<th>Wt. fraction x-mer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-mer</td>
<td>500</td>
<td>200</td>
<td>0.22</td>
</tr>
<tr>
<td>3-mer</td>
<td>0.25</td>
<td>235</td>
<td>0.25</td>
</tr>
<tr>
<td>5-mer</td>
<td>0.125</td>
<td>185</td>
<td>0.20</td>
</tr>
<tr>
<td>7-mer</td>
<td>0.063</td>
<td>126</td>
<td>0.14</td>
</tr>
<tr>
<td>9-mer</td>
<td>0.031</td>
<td>80</td>
<td>0.09</td>
</tr>
<tr>
<td>11-mer</td>
<td>0.016</td>
<td>49</td>
<td>0.05</td>
</tr>
<tr>
<td>13-mer</td>
<td>0.008</td>
<td>29</td>
<td>0.03</td>
</tr>
<tr>
<td>15-mer</td>
<td>0.004</td>
<td>17</td>
<td>0.02</td>
</tr>
<tr>
<td>17-me</td>
<td>0.002</td>
<td>9</td>
<td>0.01</td>
</tr>
</tbody>
</table>

*The sum of the mole fractions up through 17-mers represents 99.9% of the total.
Vita

The author was born in Long Island, N.Y. on May 29th, 1961. He grew up near the Long Island Sound, where he graduated from Northport High School in 1979 and enrolled at the State University of New York at Fredonia. He graduated with a Bachelors of Science degree in Chemistry, and New York State Certification to teach Chemistry at the High School level. Following graduation, he became employed as a chemist for a pharmaceutical laboratory on Long Island, New York. In 1987 the author enrolled in a Masters in Chemistry program at the Rochester Institute of Technology, and studied polymer synthesis and characterization under the advisement of Dr. Jerry Aducci. In January 1990 he entered the Ph.D. program at Virginia Polytechnic Institute and State University under the advisement of Dr. Judy S. Rifflé. During his tenure at Virginia Tech he spent two summers working in the Polycondensation Research Laboratories of Eastman Chemical Co, and presented papers in national meetings in polymer chemistry, and coauthored six publications and a patent.


John V. Facinelli