

**Synthesis and Characterization of
Phenylethynyl Terminated Poly(arylene
ether sulfone)s as Thermosetting Structural
Adhesives and Composite Matrices**

Sue Mecham

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
Chemistry

James E. McGrath, Chair
Thomas C. Ward
James W. Wolfe
John G. Dillard
John J. Lesko

April 21, 1997
Blacksburg, Virginia
Copyright 1997, Sue J. Mecham

Abstract

High temperature, solvent resistant materials which also display good mechanical properties are desired for use as aerospace structural adhesives and polymer matrix/carbon fiber composites. High molecular weight amorphous poly(arylene ether sulfone) thermoplastic materials display many of these desirable characteristics but are deficient in solvent resistance. Previous attempts to prepare poly(arylene ether) based thermosets to improve solvent resistance have been largely unsuccessful due to processibility issues from the low curing temperature and high glass transition temperature of the thermoset precursor. Incorporation of a high temperature curable ($\geq 350^{\circ}\text{C}$) endgroup such as 3-phenylethynylphenol in the synthesis of controlled molecular weight poly(arylene ether sulfone) oligomers has allowed for a large processing window prior to the exothermic cure that forms the desired networks. Control of oligomer molecular weight and backbone structure has allowed for further control of the processing, thermal transitions and adhesive properties of the thermosets.

A systematic series of phenylethynyl terminated oligomers derived from either bisphenol A, or wholly aromatic hydroquinone or biphenol has been synthesized and characterized to determine the influence of backbone structure, molecular weight, and endgroup structure on thermoset properties. The features most affected by backbone structure included thermal stability (weight loss behavior) as well as transition temperatures (T_g , T_m), and processing characteristics. Increasing molecular weight of the oligomer produced a decrease in the glass transition temperature of the network and an increase in the adhesive properties of the thermoset. Comparison of the curing behavior of the 3-phenylethynylphenol endcapped materials with other related phenylethynyl terminated compounds led to the synthesis and systematic investigation of the curing behavior of phenylethynyl endcappers in which the electronic environment in relation to the reactive ethynyl carbons was systematically varied. Electron withdrawing groups, eg. sulfone, ketone, imide on the aryl ring para to the acetylene bond enhanced the rate of cure and also appear to improve the lap shear adhesion to surface treated titanium adherands. Discussion of the background, synthesis and characterization are described in this dissertation.

Acknowledgments

I must first acknowledge my committee members, Dr. Wolfe, Dr. Ward, Dr. Lesko, Dr. Dillard and most especially my committee chair, Dr. McGrath. Without their guidance, support, and understanding this thesis would not have been possible. Their willingness to answer questions and provide information, as well as discussion and insight, was useful in many ways throughout this research and was greatly appreciated. Dr. McGrath must be particularly thanked for his continued guidance and encouragement over the many years I have worked with him. His continued efforts to provide new opportunities which broadened my experience and enhanced my abilities are very much appreciated.

The financial support of the National Science Foundation Science and Technology Center for High Performance Polymeric Adhesives and Composites was appreciated for the research as well as the stipend support from the Adhesive and Sealant Council Education Foundation through the Center for Adhesive and Sealant Science.

My family also deserves a good deal of recognition for their love and support. My mother, Dr. Judy Riffle was my inspiration

for achieving this goal and has always supported my efforts with encouragement and understanding . My husband Jeff has been my colleague, friend, and support base and co-parent to our son, Michael, for the duration of my Ph.D. research, even while conducting his own research and coursework. Jeff's and Michael's endurance of long work hours and out of town meetings made these efforts successful.

Last, but certainly not least I must thank my colleagues who have helped me in so many ways while this research was conducted. While it is impossible to name every individual who provided assistance I will attempt to acknowledge those who were an integral part of the research. For characterization assistance I must thank Mr. Tom Glass (NMR), Dr. Limin Dong and Dr. Qing Ji (GPC), Dr. Venkat Vasudevan and Dr. M. Sankarapandian (adhesion), Mr. Todd Bullions (composite testing), Mrs. Elizabeth Webster (DSC) and Mr. Mark Muggli (DMA). I also trained and supervised a number of undergraduates in research, during the course of my research, and their efforts were also used in conjunction with my own to provide the results included in this dissertation. I thank Maggie (Bobbitt) Bump, Jason Wall and Mical Pallack as well as Ms. Yunhui Sun for her assistance in the laboratory, especially during my

pregnancy. My colleague Dr. A. Ayambem is continuing the research efforts and his input has been greatly appreciated as well. All of my labmates over the years have been generous in sharing equipment and discussions with me on various aspects of research and I feel very fortunate to have worked with them.

Table of Contents

Table of Figures.....	xiv
Table of Tables.....	xviii
Chapter 1 Introduction.....	1
Chapter 2 Literature Review.....	6
2.1 Introduction.....	6
2.2 Synthesis of Poly(arylene ether sulfone)s and Related Materials.....	7
2.2.1 - Poly(arylene ether sulfone)s.....	7
2.2.2 - Nucleophilic Aromatic Substitution with Emphasis on Important Variables.....	7
2.2.2.1 - The Activating Group.....	8
2.2.2.2 - The Leaving Group.....	10
2.2.2.3 - The Nucleophile.....	11
2.2.2.4 - The Solvent.....	12
2.2.2.5 - Water.....	13
2.2.3 - Synthesis of Poly(arylene ether sulfone)s via Nucleophilic Aromatic Substitution.....	15
2.2.3.1 - Strong Base Synthetic Route.....	17
2.2.3.2 - Weak Base Synthetic Route.....	20

2.3	Physical Characteristics of Poly(arylene ether sulfone)s.....	2 8
2.4	Thermosetting Poly(arylene ether)s.....	3 2
2.4.1	- Poly(arylene ether sulfone) Thermosets....	3 6
2.5	Network Formation Based on the Curing Reaction of the Phenylethynl Moiety.....	5 9
2.5.1	- Investigations of Phenylethynyl Model Compounds.....	6 1
2.5.2	- Investigations of Difunctional Phenylethynyl Terminated Polymers.....	7 2
Chapter 3	Experimental.....	7 7
3.1	Introduction.....	7 7
3.2	Purification of Reagents and Solvents.....	7 8
3.2.1	- Solvent Acquisition and Purification.....	7 8
3.2.1.1	- Acetic Acid.....	7 8
3.2.1.2	- Triethylamine.....	7 8
3.2.1.3	- Methanol.....	7 9
3.2.1.4	- N,N-Dimethylacetamide.....	7 9
3.2.1.5	- Toluene.....	8 0
3.2.1.6	- Chloroform.....	8 0
3.2.1.7	- Diethyl Ether.....	8 1

3.21.8 - Hexanes.....	8 1
3.2.1.9 - 1-Methyl-2-Pyrrolidinone.....	8 2
3.2.1.10 - Dimethyl Sulfoxide.....	8 2
3.2.1.11 - Chlorobenzene.....	8 3
3.2.2 - Reagent Acquisition and Purification.....	8 3
3.2.2.1 - 3-Bromophenol.....	8 3
3.2.2.2 - Phenylacetylene.....	8 4
3.2.2.3 - .Bis(triphenylphosphine) Palladium(II) chloride.....	8 4
3.2.2.4 - Copper Iodide.....	8 5
3.2.2.5 - Triphenylphosphine.....	8 5
3.2.2.6 - Potassium Carbonate.....	8 6
3.2. 2.7 - 4-Bromobenzene.....	8 6
3.2.2.8 - 4-Fluorobenzenesulfonylchloride..	8 7
3.2.2.9 - Aluminum Chloride.....	8 7
3.2.2.10 - 4-Phenylethynylphthalic Anhdride.....	8 8
3.2.2.11 - 4-Aminophenol.....	8 8
3.3 Synthesis, Acquisition and Purification of Monomers.....	8 9
3.3.1 - Monofunctional Endcappers.....	8 9

3.3.1.1	- 3-Phenylethynylphenol.....	8 9
3.3.1.2	- 4-Fluoro-4'-Phenylethynyl- benzophenone.....	9 2
3.3.1.3	- 4-Fluoro-4'-Phenylethynyl- diphenylsulfone.....	9 3
3.3.1.4	- Phenylethynylphthalimidophenol.....	9 6
3.3.1.5	- Bisphenol A.....	9 7
3.3.1.6	- Hydroquinone.....	9 8
3.3.1.7	- 4,4'-Biphenol.....	9 8
3.3.1.8	- 4,4'-Dichlorodiphenylsulfone.....	9 9
3.4	Phenylethynyl Terminated Poly(arylene ether sulfone)s.....	1 0 0
3.4.1	- Molecular Weight and End-group Control in Polymers.....	1 0 0
3.4.2	- Synthesis of a Phenylethynyl Terminated Poly(arylene ether sulfone) Via Potassium Carbonate.....	1 0 1
3.4.3	- Synthesis of a Phenylethynyl Terminated Poly(arylene ether sulfone) Via Sodium Hydroxide.....	1 0 4
3.5	Manufacture of Composite Panel.....	1 0 9
3.6	Characterization.....	1 1 0
3.6.1	- Nuclear Magnetic Resonance Spectroscopy (NMR).....	1 1 0

3.6.1.1 - ¹ H NMR.....	1 1 0
3.6.1.2 - Quantitative ¹³ C NMR.....	1 1 1
3.6.2 - Gel Permeation Chromatography.....	1 1 1
3.6.3 - Potentiometric Titrations.....	1 1 2
3.6.4 - Differential Scanning Calorimetry.....	1 1 2
3.6.5 - Thermogravimetric Analysis.....	1 1 3
3.6.6 - Melt Rheology.....	1 1 3
3.6.7 - Single Lap Shear Measurements.....	1 1 4
3.6.8 -Infrared Spectroscopy.....	1 1 4
3.6.9 - Flexural Testing of Composite Panels.....	1 1 5
3.6.10 - Short Beam Shear Testing of Composite Panels.....	1 1 6
3.6.11 - Dynamic Mechanical Thermal Analysis....	1 1 7
3.6.12 - Soxhlet Extraction.....	1 1 7
Chapter 4 Results and Discussion.....	1 1 9
4.1 Introduction.....	1 1 9
4.2 Characterization of Phenylethynyl Endcappers...	1 2 0
4.2.1 - 3-Phenylethynylphenol (PEP).....	1 2 0
4.2.2 - 4-Fluoro-4'-Phenylethynylbenzophenone (FPEB).....	1 2 5

4.2.3	- 4-Fluoro-4'-Phenylethynyldiphenylsulfone (PEFDPS).....	1 2 8
4.2.4	- Phenylethynylphthalimidophenol (PEPIP)....	1 3 3
4.2.5	- Comparison of the Structures of the Monofunctional Endcapper Molecules.....	1 3 7
4.3	Molecular Weight and Endcapping of 3-Phenylethynylphenol Terminated Oligomers.....	1 4 2
4.3.1	- Molecular Weight by Endgroup Analysis.....	1 4 2
4.3.2	- Molecular Weight by Size Exclusion Chromatography.....	1 5 1
4.3.3	- Correlation of ¹³ C NMR and GPC Results.....	1 5 8
4.4	Curing of Phenylethynyl Oligomers: Network Formation.....	1 6 1
4.4.1	- Rheology.....	1 6 1
4.4.2	- Extent of Cure.....	1 6 7
4.5	Thermal Analysis of Oligomers and Thermosets.....	1 7 0
4.5.1	- Thermal Stability.....	1 7 0
4.5.2	- Thermal Transitions of Oligomers.....	1 7 4
4.5.3	- Thermal Transitions of Thermosets.....	1 8 1
4.6	Adhesive Properties of Thermosets.....	1 8 6
4.7	Mechanical Properties of Composite Panel.....	1 9 1

4.8	Oligomers Terminated with Different Phenylethynyl Endcappers.....	198
4.8.1	- Characterization of the 5,000 g/mole Phenylethynyl Terminated Oligomers.....	199
4.8.2	- Kinetic Study of Phenylethynyl Terminated Poly(arylene ether sulfone)s by FTIR.....	209
Chapter 5	Conclusions.....	220
Chapter 6	References.....	222

Table of Figures

Figure 2.1-S _N Ar Mechanism.....	9
Figure 2.2-Common Polar AproticSolvents.....	14
Figure 2.3-Generic Nucleophilic Aromatic Substitution Polymerization.....	16
Figure 2.4-Nucleophilic Aromatic Substitution Polymerization via Bisphenate.....	18
Figure 2.5-Synthesis of Bisphenol A Polysulfone via the Weak Base Method of Nucleophilic Aromatic Substitution Polymerization.....	22
Figure 2.6-Reactions of Potassium Carbonate in the Formation of Phenates and Water.....	23
Figure 2.7-Commercial Polysulfone Backbones.....	30
Figure 3.1-Synthesis of Phenylethynylphenol Terminated Poly(arylene ether sulfone) Oligomers with Potassium Carbonate.....	102
Figure 3.2-Synthesis of Phenylethynyl Terminated Poly(arylene ether sulfone) Using Sodium Hydroxide as the Base.....	106
Figure 4.1-Synthesis of 3-Phenylethynylphenol.....	121
Figure 4.2- ¹ H NMR Spectrum of 3-Phenylethynylphenol in Deuterated Chloroform.....	123
Figure 4.3-FTIR Spectrum of 3-Phenylethynylphenol (KBr Pellet).....	124
Figure 4.4- ¹ H NMR Spectrum of 4-Fluoro-4'-Phenylethynyl- benzophenone in Deuterated Chloroform.....	126

Figure 4.5-FTIR Spectrum of 4-Fluoro-4'-Phenylethynyl-benzophenone (KBr Pellet).....	1 2 7
Figure 4.6-Synthesis of 4-Fluoro-4'-Phenylethynyldiphenylsulfone.....	1 3 0
Figure 4.7- ¹ H NMR Spectrum of 4-Fluoro-4'-Phenylethynyldiphenylsulfone in Deuterated Chloroform.....	1 3 1
Figure 4.8-FTIR Spectrum of 4-Fluoro-4'-Phenylethynyldiphenylsulfone (KBr Pellet).....	1 3 2
Figure 4.9-Synthesis of 3-Phenylethynylphthalimidophenol...	1 3 4
Figure 4.10- ¹ H NMR Spectrum of Phenylethynylphthalimidophenol in Deruterated Chloroform.....	1 3 5
Figure 4.11-FTIR Spectrum of Phenylethynylphthalimidophenol (KBr Pellet).....	1 3 6
Figure 4.12- ¹³ C NMR of the Ethynyl Region of Phenylethynyl Monofunctional Endcappers.....	1 3 8
Figure 4.13- ¹³ C NMR Spectrum of a 3,000 g/mole Phenylethynyl Terminated Hydroquinone Based Poly(arylene ether sulfone).....	1 4 4
Figure 4.14- ¹³ C NMR Spectrum of a 3,000 g/mole Phenylethynyl Terminated 4,4'-Biphenol Based Poly(arylene ether sulfone).....	1 4 5
Figure 4.15- ¹³ C NMR Spectrum of a 3,000 g/mole Phenylethynyl Terminated Bisphenol A Based Poly(arylene ether sulfone).....	1 4 6
Figure 4.16- ¹³ C NMR Spectrum of a 5,000 g/mole Phenylethynyl Terminated 50:50 Hydroquinone:4,4'-Biphenol Based Poly(arylene ether sulfone).....	1 4 7

Figure 4.17-Size Exclusion Chromatogram (SEC) of a 5,000 g/mole Phenylethynyl Terminated 70:30 Hydroquinone: 4,4'-Biphenol Poly(arylene ether sulfone) Copolymer Using a Differential Viscosity Detector.....	153
Figure 4.18-SEC of a 5,000 g/mole Phenylethynyl Terminated 70:30 Hydroquinone:4,4'-Biphenol Poly(arylene ether sulfone) Copolymer Using a Refractive Index Detector.....	154
Figure 4.19-Molecular Weight Distribution of a 5,000 g/mole Phenylethynyl Terminated 70:30 Hydroquinone:4,4'-Biphenol Poly(arylene ether sulfone) Copolymer.....	155
Figure 4.20-Experimental M_n vs. Target M_n for a Series of Phenylethynyl Terminated Poly(arylene ether sulfone) Oligomers.....	160
Figure 4.21-Melt Viscosity vs. Temperature for a 5,000 g/mole Phenylethynyl Terminated Poly(arylene ether sulfone) at a Heating Rate of 3°C/min.....	162
Figure 4.22-Melt Viscosity vs. Temperature for a 2,000 g/mole Phenylethynyl Terminated Poly(ether sulfone) at a Heating Rate of 3°C/min.....	164
Figure 4.23-Melt Viscosity vs. Time for a 5,000 g/mole Phenylethynyl Terminated Poly(arylene ether sulfone) Under Isothermal Conditions of 350°C and 380°C.....	166
Figure 4.24-Thermogravimetric Analysis of Uncured 5,000 g/mole Phenylethynyl Terminated Poly(arylene ether sulfone) Oligomers Based on Different Bisphenols at 10°C/min in Air.....	171

Figure 4.25-DSC Thermograms of Semi-crystalline 5,000 g/mole Phenylethynyl Terminated Poly(arylene ether sulfone) Oligomers from the First Heat at 10°C/min in Nitrogen.....	180
Figure 4.26-Picture of a Single Lap Shear Bond.....	187
Figure 4.27- Comparative Flexural Strengths of AS4-PW-3k composite Panels with a Variety of Thermosetting Resins.....	194
Figure 4.28- Ethynyl Carbon Shifts in the ¹³ C NMR of Phenyl- ethynyl Terminated Bisphenol A Based Oligomers.....	202
Figure 4.29-FTIR Spectra of a 5,000 g/mole Bisphenol A Based Phenylethynyl Terminated Oligomer Endcapped with a Sulfone Based Endcapper (PEFDPS) Taken Every 1 minute at 350°C.....	211
Figure 4.30-Disappearance of the Ethynyl Stretch with Time in a PEFDPS Terminated Poly(arylene ether sulfone) at 320°C Assuming First Order Kinetics.....	213
Figure 4.31- Disappearance of the Ethynyl Stretch with Time in a PEFDPS Terminated Poly(arylene ether sulfone) at 350°C Assuming First Order Kinetics.....	214
Figure 4.32-FTIR Spectra of a 5,000 g/mole Bisphenol A Based Phenylethynyl Terminated Oligomer Endcapped with a Carbonyl Based Endcapper (FPEB) Taken Every 5 minutes at 350°C.....	215
Figure 4.33- Disappearance of the Ethynyl Stretch with Time in a FPEB Terminated Poly(arylene ether sulfone) at 350°C Assuming First Order Kinetics.....	216

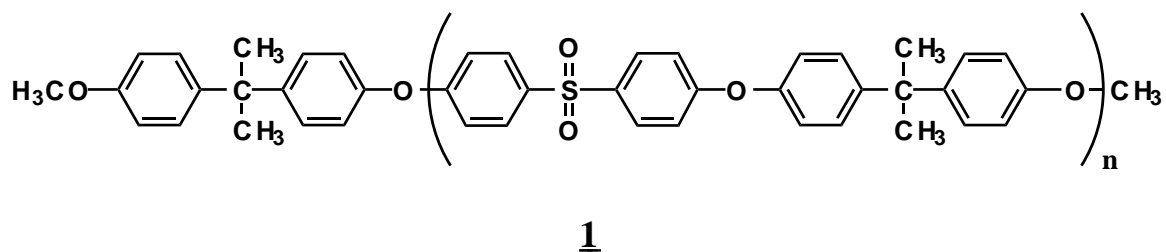
Table of Tables

Table 2.1-Reactive Groups for High-Performance Thermosets	34
Table 2.2-Half-lives of the Curing Reaction of Phenylethynyl Model Compounds Measured by HPLC.....	71
Table 4.1- ¹³ C NMR Shift Values for Ethynyl Carbons of Diphenylacetylene Derivatives.....	140
Table 4.2-Average M _n Values from ¹³ C NMR of 3-Phenylethynylphenol Terminated Oligomers.....	149
Table 4.3-Calculated Molecular Weight Numbers from GPC for Phenylethynyl Terminated Poly(arylene ether sulfone) Oligomers.....	157
Table 4.4-Gel Fractions of Cured Poly(arylene ether sulfone) Oligomers from Soxhlet Extraction with Chloroform for 4 Days.....	168
Table 4.5-5% Weight Loss for Phenylethynyl Terminated Poly(arylene ether sulfone) Oligomers Measured from TGA at 10°C/min in Air.....	173
Table 4.6-Thermal Transition Temperatures of Phenylethynyl Terminated Poly(arylene ether sulfone) Oligomers from DSC at 10°C/min in Nitrogen.....	175
Table 4.7-Heats of Fusion of Semi-crystalline 5,000 g/mole Phenylethynyl Terminated Poly(arylene ether sulfone) Oligomers from the First Heat at 10°C/min. in Nitrogen.....	180
Table 4.8-Glass Transition Temperatures of Cured Phenylethynyl Poly(arylene ether sulfone)s from the Second Heat of the DSC at 10°C/min in Nitrogen.....	182
Table 4.9-Glass Transition Temperatures of Cured Phenylethynyl Poly(arylene ether sulfone)s from DMA at 1°C/min.....	184

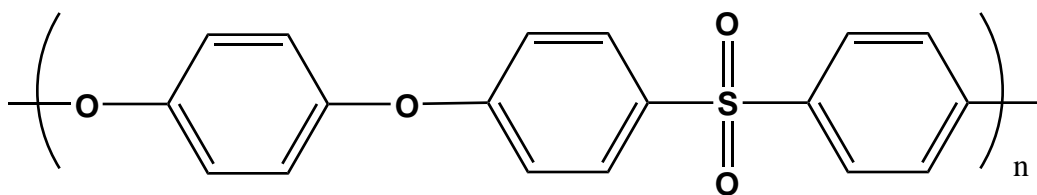
Table 4.10-Single Lap Shear Results for Cured Phenylethynyl Poly(arylene ether sulfone)s.....	190
Table 4.11-Warp Flexural Test (ASTM D 790-92) Results on AS4-PW-3k Carbon Fabric Composite Panels.....	196
Table 4.12-Molecular Weight Results for 5,000 g/mole Bisphenol A Based Oligomers Endcapped with a Series of Phenylethynyl Endcappers.....	200
Table 4.13- ¹³ C NMR Shifts of Ethynyl Carbons in Phenylethynyl Terminated Bisphenol A Based Poly(arylene ether sulfone)s.....	203
Table 4.14-Thermal and Cure Characteristics of Bisphenol A Based Oligomers Terminated with Different Phenylethynyl Endcappers.....	205
Table 4.15-Single Lap Shear Results for Cured Bisphenol A Based Oligomers with Different Phenylethynyl Endcappers.....	208
Table 4.16- First Order Rate Constants for Phenylethynyl Terminated Oligomers Cured in the FTIR.....	218

Chapter 1 Introduction

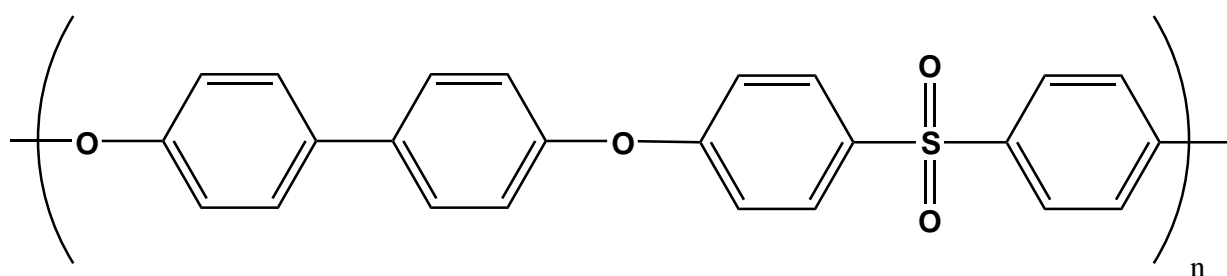
Poly(arylene ether sulfones)s^{1,2}, such as **1** display a variety of desirable characteristics including durability, thermal, hydrolytic and dimensional stability, low coefficient of thermal expansion, retention of modulus to temperatures approaching T_g and radiation resistance. However, this class of



materials has not been considered as a serious candidate for many aerospace structural adhesive and composite applications due to the poor solvent resistance of the amorphous thermoplastic material. Aromatic based polyarylethers or poly(arylene ether)s with backbone structures **2** and **3** have some improved properties over **1**, including increased glass transition temperatures, greater resistance to thermal and radiation degradation and increased solvent resistance due to the presence of semi-crystalline regions.³ These improved properties may still be insufficient for aerospace structural applications which require high performance materials which can perform at temperatures in excess of 200°C and display extremely good solvent resistance.⁴⁻¹⁰

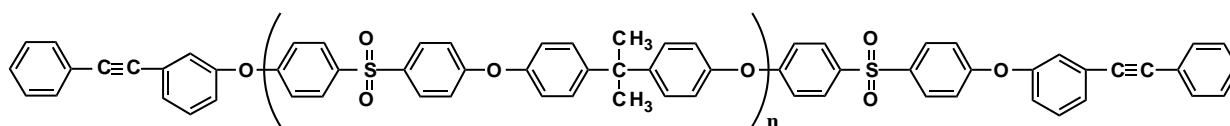


2



3

Poly(arylene ether) oligomers such as 4 can be prepared with phenylethynyl endgroups as sites for network formation. The resulting cured thermoset is expected to display most of the desirable properties of the thermoplastic analog as



4

well as very good solvent resistance. The phenylethynyl moiety undergoes an exothermic curing reaction at temperatures above 350°C.¹¹⁻¹⁴

Since the oligomeric glass transition temperature value can be designed to be below 200°C there is a desirable large melt processing window for these materials between T_g and T_{cure} . Moreover, the melt viscosity of some oligomeric poly(arylene ether)s is very low, between 250°C and 350°C, suggesting applicability to processing techniques such as resin infusion (RIM) and/or resin transfer molding (RTM) which are attractive methodologies for the economical manufacture of polymer matrix/carbon fiber composites.

It has been demonstrated during recent years that controlled molecular weight poly(arylene ether sulfone) oligomers with both homopolymer and copolymer backbone structures can be prepared with phenylethynyl endgroups as sites for network formation.^{12,15-19} **All of the monomers excluding the mono-functional endcapping agent are commercially available in monomer grade purity.** The end-capping agent most used to incorporate the phenylethynyl end-groups is 3-phenylethynylphenol, which can be synthesized through the coupling of 3-iodo or 3-bromo phenyl acetate and phenyl acetylene. The acetate group can be subsequently cleaved with base to afford the desired 3-phenylethynylphenol. The synthesis of this material has been previously published.¹³

This dissertation has investigated the synthesis and characterization of a variety of phenylethynyl terminated polyarylether sulfones. The original series consisted of **4** and the homopolymer backbones of **2** and **3** with phenylethynyl endgroups identical to **4**. A range of oligomer molecular weights was studied for each materials system. Next, phenylethynyl copolymers with the same endgroups as **4**, but with varying ratios of the two wholly aromatic bisphenols used in the synthesis of **2** and **3** were prepared. The third series incorporated slightly different endgroups which probed the influence of the local electronic structure on reactivity and otherwise produced a series of polymers analogous to **4**. This was achieved by using a series of phenylethynyl endcapping agents as the monofunctional endcapping agent in the synthesis of the polyarylethers. The synthesis and characterization of the monofunctional endcappers are also discussed.

The small molecules synthesized during this research have been characterized with regard to their molecular structure and purity. The oligomeric materials were also characterized for structure and molecular weight as well as for selected physical characteristics such as thermal behavior.

The main objective of this research was to synthesize, characterize and investigate the utility of these materials as structural adhesives for titanium and carbon fiber composite matrices. Thus, the curing of the oligomeric precursor

materials into thermoset networks was accomplished and critical properties of the network materials were determined. Measurements of adhesive properties by single lap shear tests are presented and processing behavior using parallel plate methods have been examined. Research into the area of composite manufacture and characterization has been initiated and some initial results will be presented.

The synthesis of the controlled molecular weight oligomers with varying backbones , molecular weights and phenylethynyl endgroups has allowed for systematic property data to be obtained. The measured properties has provided data for an initial evaluation of this class of thermosets for adhesive and composite applications. In addition a clearer understanding of the structure property relationships provides some insight for property improvement and refinement through structural and molecular weight variations.

Chapter 2- LITERATURE REVIEW

2.1 Introduction

The material discussed in this section begins with a discussion of the basic material synthesis and properties of polyarylene ethers. The nucleophilic aromatic substitution mechanism used in this research will be discussed in detail. The properties of the thermoplastic materials will also be briefly discussed.

This research focuses on new thermosetting polyarylether sulfones and also reviews existing thermosetting polyarylether sulfones. The chapter includes a review of phenylethynyl terminated polymers, with emphasis on the studies which include some investigation or interpretation of the curing mechanism.

2.2 Synthesis of Poly(arylene ether sulfone)s and Related Materials

2.2.1 Poly(arylene ether sulfone)s

Poly(arylene ether sulfone)s are a class of tough ductile engineering thermoplastic materials which display many desirable properties, including good hydrolytic, oxidative, and thermal stability. These materials have been synthesized via a variety of different routes. The most important commercial routes being nucleophilic aromatic substitution^{6,7,9,12,20-29} and, to a lesser extent, electrophilic aromatic substitution^{23,30-37}. The nucleophilic aromatic substitution route to poly(arylene ether sulfone)s is currently utilized commercially by Amoco Chemical in the synthesis of their bisphenol A based polysulfone (**1**), UDEL[®] and by the BASF Corporation. Nucleophilic aromatic substitution is also the synthetic route to the materials produced in this research, therefore the background for this mechanism will be discussed herein.

2.2.2 Nucleophilic Aromatic Substitution with Emphasis on Important Variables

There are four important mechanisms for aromatic nucleophilic substitution^{38,39}. The most important of which, the S_NAr, is applicable to poly(arylene ether sulfone)s. The general S_NAr mechanism is shown in figure

2.1. Step one involves the attack of the nucleophile on the activated site to form a resonance stabilized arenium ion intermediate, which is usually the rate determining step. Step two involves the departure of the leaving group and is usually fast and results in reformation of aromaticity in the ring.

2.2.2.1 The Activating Group

The presence of an electron withdrawing group in the ortho and/or para positions stabilizes the intermediate formed in step one; however, substitution at the ortho position can sterically hinder the attack of the nucleophile. A electron withdrawing group such as a nitro group stabilizes the intermediate by forming a Meisenheimer salt, **5**, named after its discoverer⁴⁰. The structure of intermediates such as **5** have been confirmed by NMR⁴¹ and X-ray crystallography⁴². The S_NAr mechanism is supported by the fact that these intermediates have been isolated and that the presence of the electron withdrawing group in the para position accelerates the rate of the reaction by stabilizing the intermediate formed in the rate determining step. The approximate order of electron withdrawing power corresponds to the

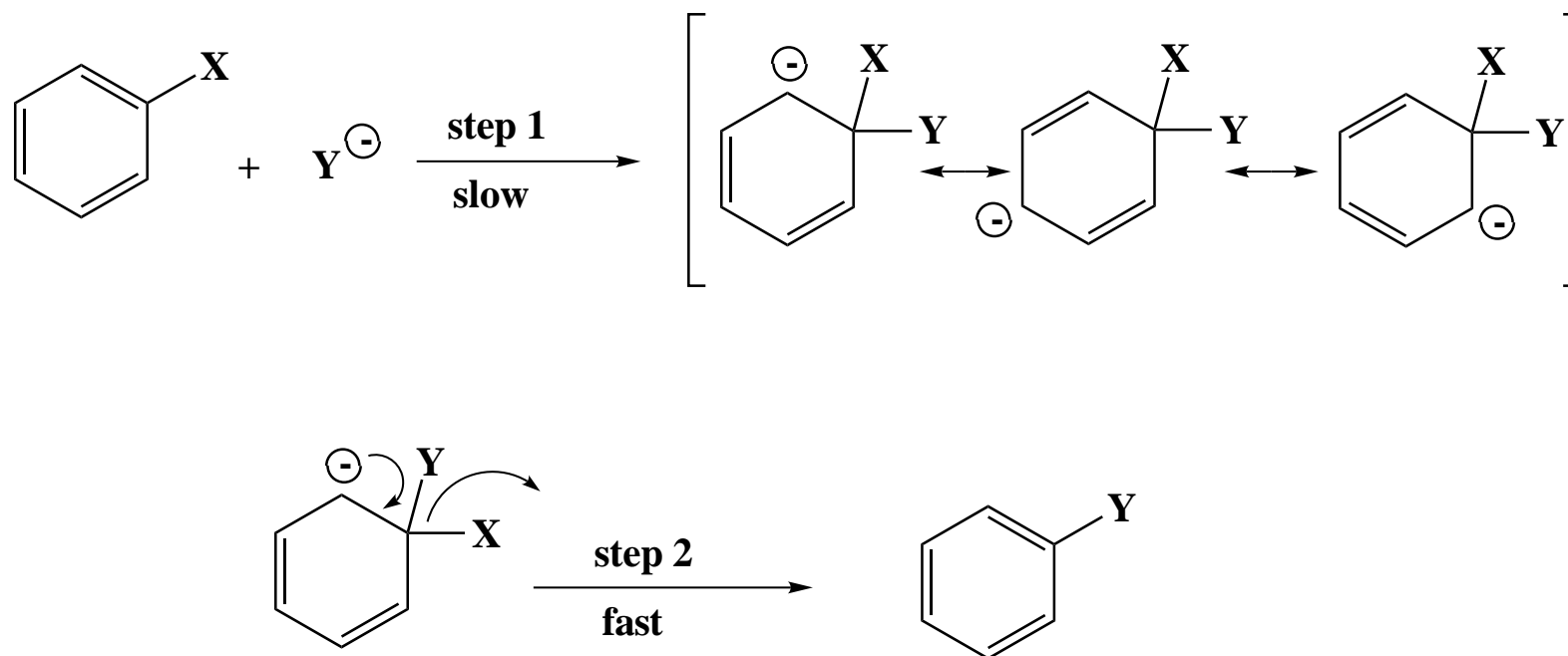
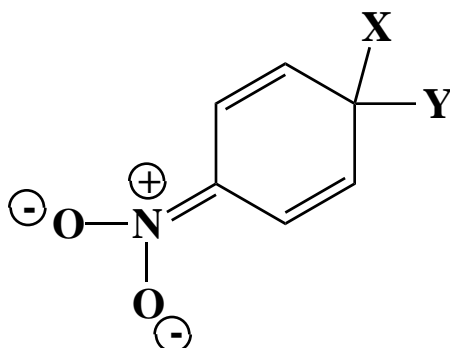


Figure 2.1 S_NAr Mechanism³⁹



5

deactivating power of the substituent and has been observed^{38,43} to be: $\text{NO} > \text{NO}_2 > \text{SO}_2\text{Me} > \text{CF}_3 > \text{CN} > \text{CHO} > \text{COR} > \text{COOH} > \text{Br} > \text{Cl} > \text{I} > \text{H} > \text{F} > \text{CMe}_3 > \text{Me} > \text{OMe} > \text{NMe}_2 > \text{OH} > \text{NH}_2$. Nitro, sulfone and ketone groups are common activating groups utilized in the synthesis of polyarylene ethers.

2.2.2.2 The Leaving Group

The leaving group (X^-) is an important variable in the nucleophilic aromatic substitution polymerization of polyarylene ether sulfones. Bunnett⁴⁴ reported that the rate of the reaction was dependent on the leaving group in the order of $\text{F} \gg \text{Cl} \geq \text{Br} \geq \text{I}$ for the halogen series. This is despite the fact that the bond strengths for carbon-halogen bonds decrease in the same order. One concludes that the leaving group is not lost in the rate determining step and that

the breaking of that bond is not rate determining. The reason why it has an effect on the rate of the reaction at all is because the leaving group has an electronic effect on the activated carbon which is attacked in the rate determining step. The greater electronegativity of the fluorine atom allows it to inductively withdraw electron density from the activated carbon, further activating it to attack by a nucleophile as well as stabilizing the intermediate. In addition to the argument for electronegativity it is possible that steric effects play a role in the increase in rate. Thus, a smaller atom on the activated carbon allows for more access to that carbon for the incoming nucleophile.

2.2.2.3 The Nucleophile

The nucleophilicity of the nucleophile plays an important role in the polymerization of polyarylene ether sulfones by nucleophilic aromatic substitution. An approximate order of nucleophile strength is: $\text{ArS}^- > \text{RO}^- > \text{R}_2\text{NH}^- > \text{ArO}^- > \text{OH}^- > \text{ArNH}_2 > \text{NH}_3 > \text{I}^- > \text{Br}^- > \text{Cl}^- > \text{H}_2\text{O} > \text{ROH}$.⁴⁴ This is important in the polymerization reaction as it is vital that side reactions be avoided to obtain high molecular weight products. This order suggests that the phenoxide anion is the strongest nucleophile in the reaction with nucleophilicity above hydroxide ion, the halogens and water.

2.2.2.4 The Solvent

The choice of solvent is particularly important in the nucleophilic aromatic substitution polymerization reaction. There are three major requirements of the solvent. Firstly, it is important that the solvent not undergo any reaction with the reactants leading to side products. Next, the solvation power of the solvent must be such that all of the reactants and products have sufficient solubility to react with each other. This can be a significant problem with polymers where the reacting chain end must remain in solution even when the polymer chain has grown very large. Lastly, the solvent should be able to aid in the dissociation of the nucleophilic anion from the metal cation associated with it.

Nucleophilic substitution reactions are commonly conducted in polar aprotic solvents as opposed to protic solvents. The reason for this is that the nucleophilicity of the nucleophile is highly dependent on solvent interactions.⁴⁵ Protic solvents will highly solvate the nucleophile, thereby reducing its ability to react with the activated carbon. In the absence of protic solvents the relative nucleophilicity of anions changes, presumably due to the removal of solvation effects.^{46,47}

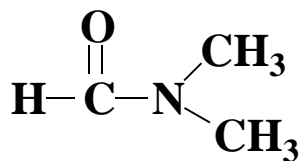
Some common polar aprotic solvents are shown in figure 2.2. These solvents not only reduce the solvation of the nucleophiles but they can enhance the

nucleophilicity of the nucleophile by strongly solvating the cations associated with the nucleophiles.⁴⁸ Solvation of the cation reduces the strength of the ionic bond allowing the nucleophile to react more easily at the activated carbon.

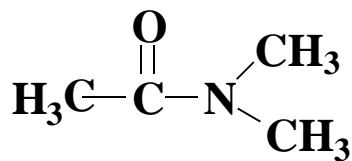
2.2.2.5 Water

Purification of the solvents is important to avoid contaminants which could undergo side reactions with the reactants, such as water. Distillation of the solvent from a suitable drying agent prior to use is a typical method to remove any water present. Water can act as a nucleophile which hydrolyzes the activated halide, reducing the yield in a small molecule reaction and disrupting the stoichiometry in a polymerization reaction.

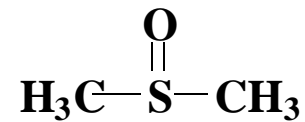
In the synthesis of poly(arylene ether sulfone)s by nucleophilic aromatic substitution, the phenoxide nucleophile may be formed through the addition of a base such as sodium hydroxide. The reaction of the base with the phenol produces 2 moles of water/mole of bisphenol, which must be removed from the reaction prior to the addition of the activated halide. The removal of the water may be accomplished using an azeotroping agent such as chlorobenzene or toluene.



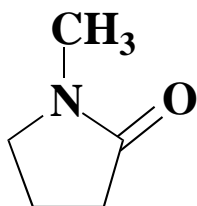
**N,N-Dimethylformamide
(DMF)**



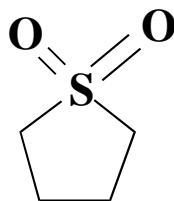
**N,N-Dimethylacetamide
(DMAc)**



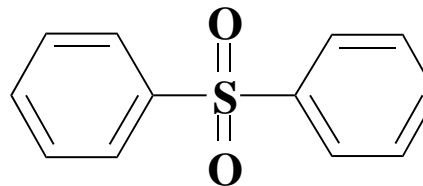
**Dimethylsulfoxide
(DMSO)**



**N-Methylpyrrolidinone
(NMP)**



Sulfolane

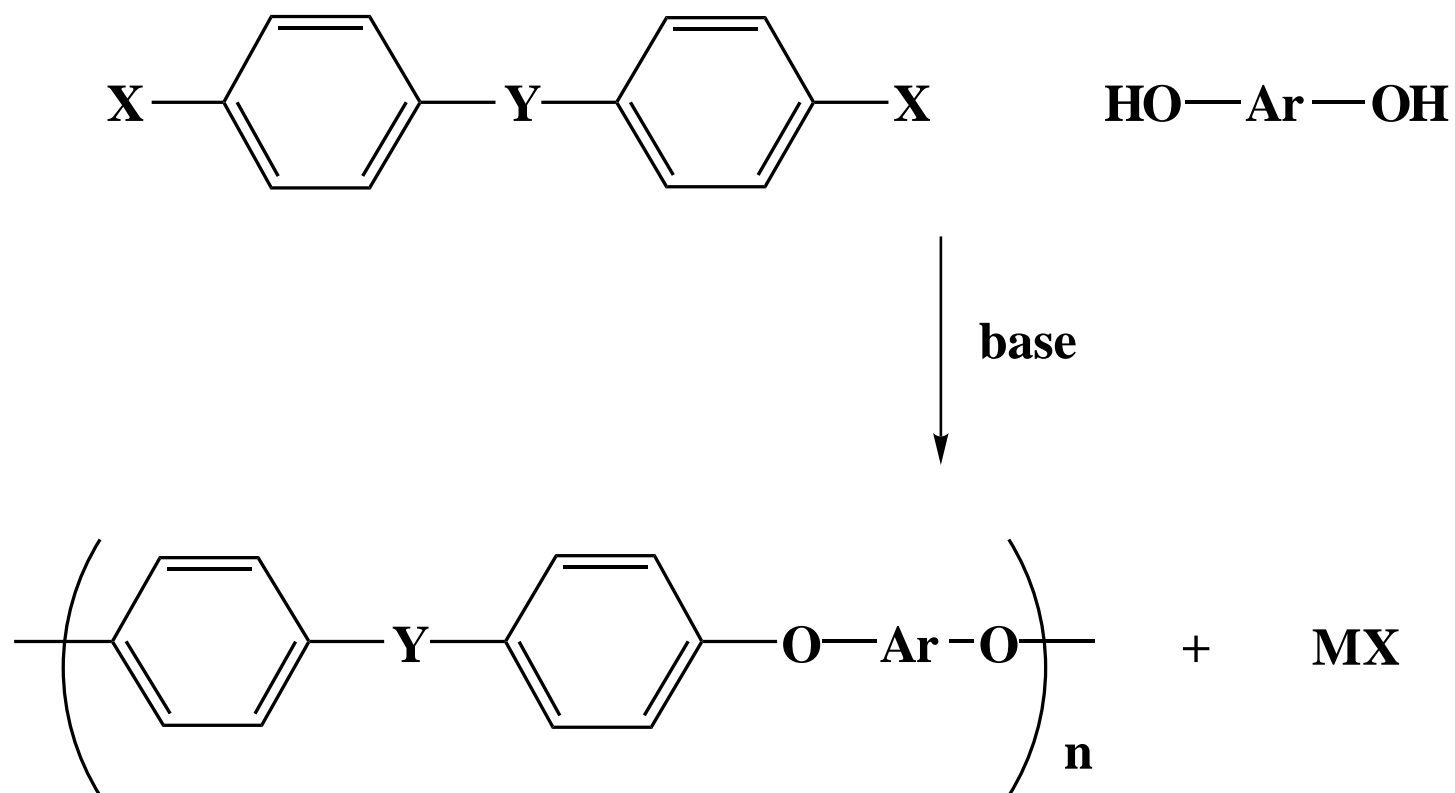


Diphenyl Sulfone

Figure 2.2 Examples of Polar Aprotic Solvents

2.2.3 Synthesis of Poly(arylene ether sulfone)s via Nucleophilic Aromatic Substitution

Polyarylene ether sulfones are prepared via nucleophilic aromatic substitution as illustrated in figure 2.3. An aromatic bisphenol is reacted with a base utilizing a metal cation, which is typically sodium or potassium. This reaction forms the phenate anion, or the diphenate with a strong base. The phenate acts as the nucleophile to displace the halide ion after nucleophilic aromatic substitution occurs on the activated dihalide to form the diaryl ether bond.



X = halide usually Cl or F

Y = activating group usually sulfone, ketone or aryl phosphine oxide

M = metal cation

Figure 2.3 Generic Nucleophilic Aromatic Substitution Polymerization

2.2.3.1 Strong Base Synthetic Route

One of the first nucleophilic aromatic routes for the synthesis of polyarylene ethers was developed by Johnson and coworkers^{9,20} and it is believed to be still used in commercial procedures today.⁴⁹ Johnson synthesized a large series of polyethers by this synthetic method and the reaction is shown in figure 2.4, using the formation of bisphenol A polysulfone as an example. They used a variety of reaction conditions and monomers and discussed the various observations made during these experiments.

Their observations for suitable solvents concluded that DMSO was the best solvent for the synthesis of almost all of the polymers. However, its usefulness was limited when the more weakly activated dichlorides or the more acidic bisphenols were used. In the cases where DMSO did not work as well one could often substitute sulfolane. In one particular case where there was a great deal of crystallization of the polymer occurs at low conversions in DMSO, it was not a problem in sulfolane.

It was previously mentioned that one of the most important features of a good solvent was the ability to solubilize both the reactants and the products. In the case of this reaction the two most difficult things to solubilize are the alkali bisphenate and the polymer. It was found that to solubilize most of the alkali bisphenates, even in DMSO, very high reaction temperatures ranging from

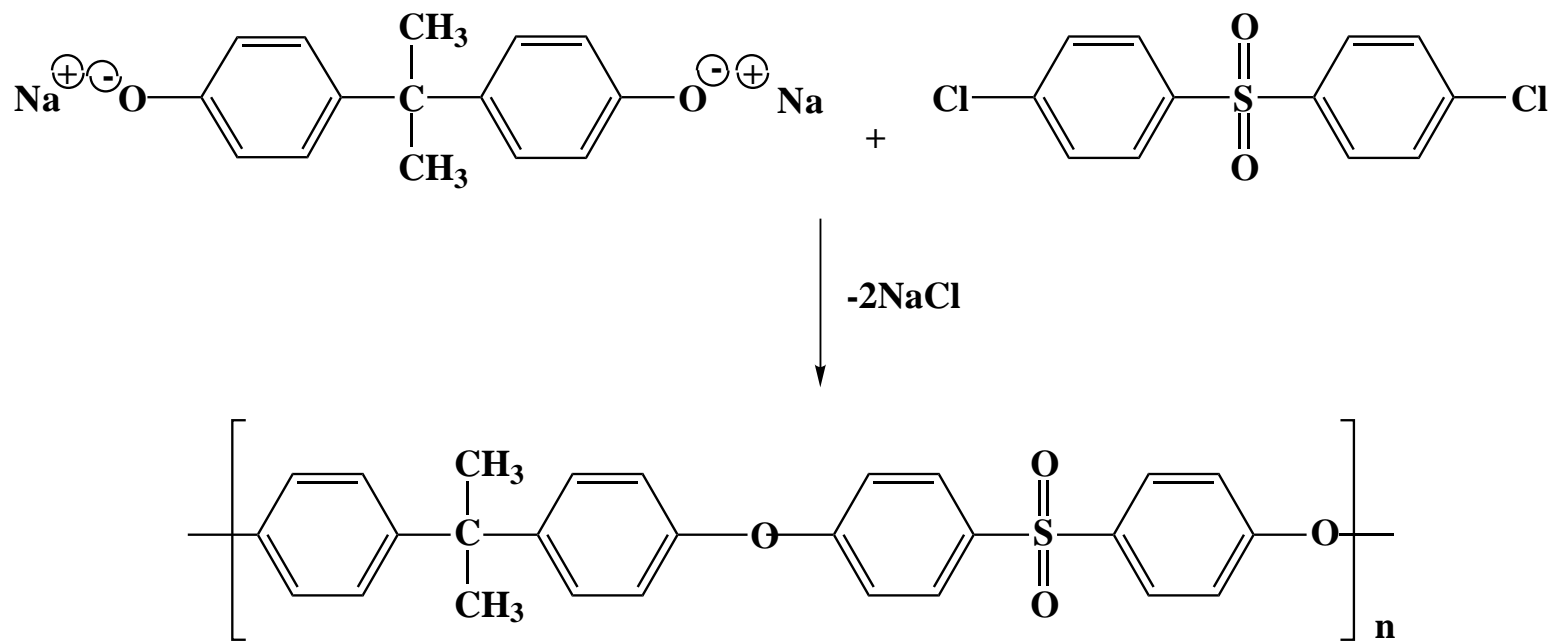


Figure 2.4 Nucleophilic Aromatic Substitution Polymerization via Bisphenate⁹

130-170°C had to be achieved. The use of sulfolane allowed even higher reaction temperatures, on the order of 230°C, to be reached when needed for the less reactive monomers.

Side reactions due to the presence of even small amounts of water had dramatic effects on the molecular weight attained. Hydrolysis of the metal phenate to produce hydroxide ion was a major side reaction. The hydroxide ion also acted as a nucleophile and displaced the activated halide, creating an endgroup of low reactivity which eventually upset the stoichiometry of the polymerization and limited molecular weight. This is believed to be the major cause of the low molecular weight achieved when water is present, because the molecular weight did not increase after the water was subsequently removed from these reactions, even when they were allowed sufficient time to achieve higher conversion. Polymer hydrolysis by the hydroxide was another possible side reaction.

Johnson and coworkers also observed that the reactivity of the various bisphenols varied inversely with their respective acidities, which is consistent with the idea that the nucleophilicity of the bisphenates increased with basicity. The sodium and potassium salts were the only ones found to have sufficient solubility in DMSO. The reactivity of the activated dihalide was dependent on both the activating group as well as the halide. Fluorinated derivatives reacted

faster than chlorinated derivatives, as long as the activating group was the same. Use of stronger activating groups such as sulfones allowed for a relatively fast reaction with Cl groups as well as F groups.

The main disadvantage to this system was the susceptibility of side reactions necessitating very careful control of the stoichiometry in the prepolymerization step involving formation of the reactive phenate and quantitative removal of water prior to addition of the activated dihalide in a second step. One important feature though was the very short reaction times required to reach high molecular weight which could be achieved after the addition of the activated dihalide. These reaction times being on the order of 1 hour for the formation of the main commercial material **1** which has the trade name UDEL[®]. Johnson and coworkers found that, depending on the reactivities of the bisphenates, reaction times to achieve high molecular weight with 4,4'-dichlorodiphenylsulfone ranged from 1-10 hours.

2.2.3.2 Weak Base Route

The initial literature available on the weak base route to nucleophilic aromatic substitution polymerization of poly(arylene ether sulfone)s is found primarily in patents.⁵⁰⁻⁵³ McGrath and coworkers⁷ investigated the anhydrous potassium carbonate/N,N'-dimethylacetamide route in 1979^{54,55} and in 1984 and

reported that this method could serve to avoid the previously mentioned problems with monomer and polymer hydrolysis and bisphenate insolubility.

McGrath and coworkers synthesized polyarylene ether sulfones through the method shown in figure 2.5 which illustrates the synthesis of bisphenol A polysulfone as an example. N,N'-dimethylacetamide (DMAc) was used as the polar aprotic solvent and toluene was utilized to azeotropically remove water in the reaction which could be present in the system and also arises from the disproportionation of potassium bicarbonate. The potassium carbonate can undergo a number of reactions to produce phenate and water, which are summarized in figure 2.6.⁷ They were able to obtain high molecular weight polymers as well as controlled molecular weight polymer through the use of a slight excess of the bisphenol.

High molecular weight polymers were obtained when a modest excess (10-20%) of base was used but the molecular weight was found to be lower when less than the stoichiometric amount was used, possibly due to less than the calculated amount of phenoxide being formed. It was determined that even the use of an excess amount of potassium carbonate did not cause hydrolysis of the activated dihalide monomer, 4,4'-dichlorodiphenylsulfone, or the polymer chain under the

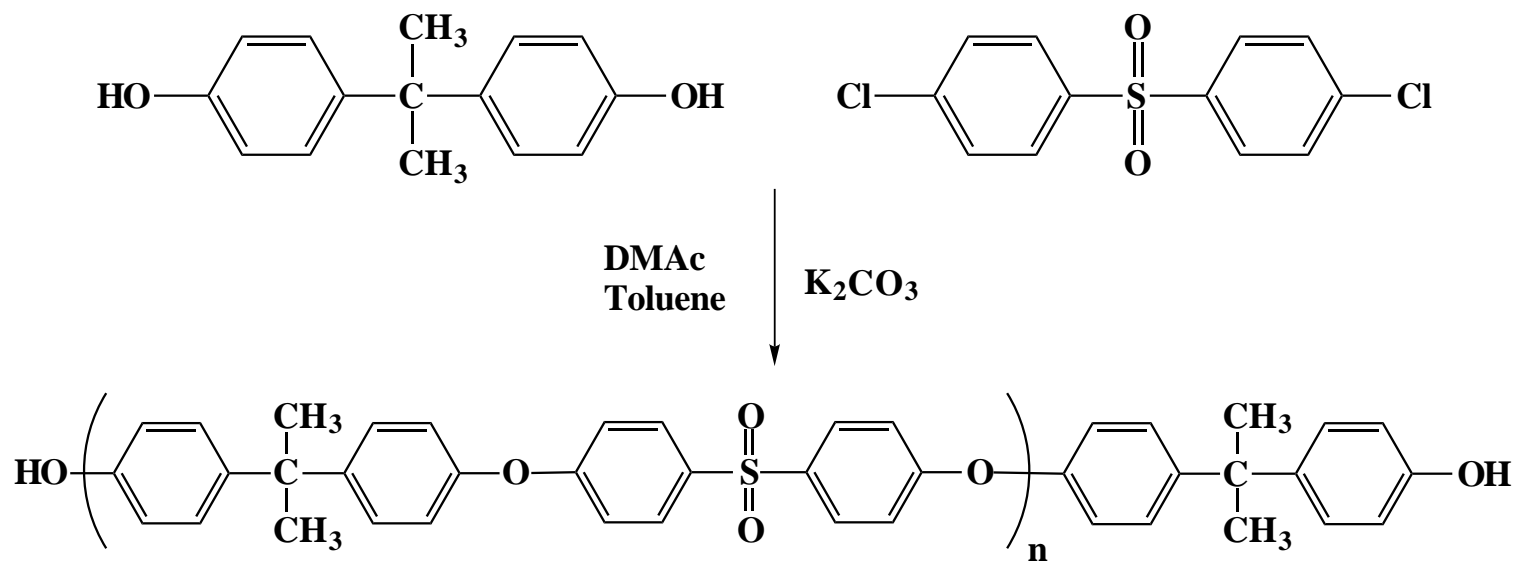


Figure 2.5 **Synthesis of Bisphenol A Polysulfone via the Weak Base Method of Nucleophilic Aromatic Substitution Polymerization**

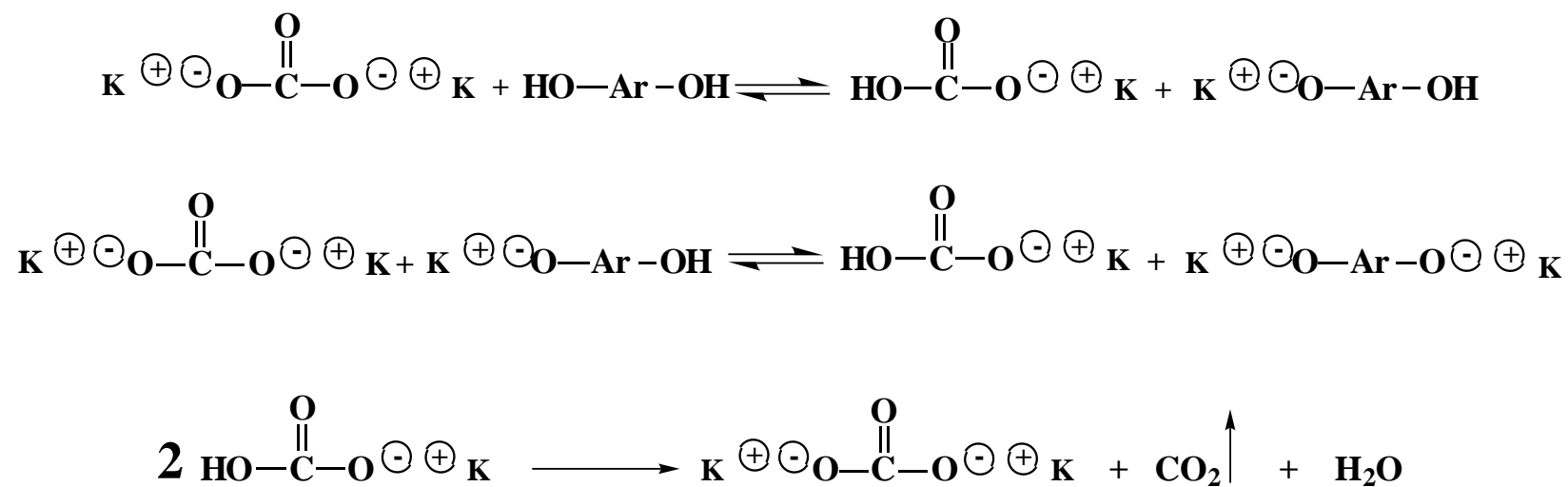


Figure 2.6 Reactions of Potassium Carbonate in the Formation of Phenates and Water⁷

conditions examined. One likely reason for this is that the concentrations of base and phenate were found to be dependent on the reaction conditions. The solubility of base was dependant on the reaction temperature, which in turn was a function of the solvent composition due to the azeotrope. At 150°C which was a typical temperature used for the bulk of the polymerization the solvent composition was determined to be 85:15 DMAc:toluene and the total amount of base in solution was determined to be 0.04 g/L. When the reaction temperature was increased to 160°C the total concentration of base increased to 0.7 g/L which was still significantly lower than the amount of base added into the reaction. The observed heterogeneous nature of this reaction has consequences on the kinetics of the reaction and is likely the reason for the extended reaction times which were estimated to be about 10 times that of the dimethylsulfoxide/sodium hydroxide route for the synthesis of bisphenol A polysulfone.

The dimethylsulfoxide/sodium hydroxide route to the synthesis of bisphenol A polysulfone was second order with respect to the concentration of the functional groups.⁵⁶ The potassium carbonate/N,N'-dimethylacetamide route did to not precisely follow the same second order kinetics, probably because of incomplete formation of the phenoxide due to base insolubility or insolubility of diphenate formed in situ. The presence of both phenate and unreacted bisphenol

in solution increases the likelihood that the nucleophilicity of the phenate will be reduced, due to hydrogen bonding with free phenolic functionality.

The solubility of the base was temperature dependent. The time necessary to achieve high molecular weight was also highly temperature dependent and likely related to the solubility issue. It was found that 10 hours at 157°C allowed the formation of high molecular weight polymer while after 10 hours at 140°C only very low molecular weight species were obtained.

Kinetic studies conducted more recently by Priddy⁵⁷ on a model compound derived from bisphenol A and monochlorodiphenylsulfone, indicated that the potassium carbonate did not easily form the diphenate of bisphenol A. Typical polymerization conditions for each of the two types of bases were utilized. Samples were taken with time and immediately quenched with excess acetic acid to protonate any phenates which were present. Once one substitution had taken place on the bisphenol, a monosubstituted product was obtained. Similarly, a disubstituted product was obtained after both phenols were substituted. The reaction conducted using potassium hydroxide as the base was observed to form both the monosubstituted and the disubstituted products almost immediately, indicating that the diphenate must be essentially present from the beginning of the reaction. Obviously, this is true as the diphenate must be formed in the reaction before the activated halide is even added. The reaction

conducted using potassium carbonate gave only monosubstituted product for the first 100 minutes. Also the initial rate of formation of the disubstituted product was much smaller than the initial rate of formation of the monosubstituted product. At around 300 minutes reaction time the amount of disubstituted product increased dramatically corresponding to a dramatic decrease in the amount of monosubstituted product present in the reaction. This is reasonable evidence that the ability of the weak base to form the diphenate is limited as it took a good deal of time to form the disubstituted products. It is likely that the second phenate is not formed until the first one has reacted to form an ether bond.

This data shed more light on the subject of why the weak base route does not quantitatively follow second order kinetics. The second order kinetics of the strong base reaction is dependent on the concentrations of the activated dihalide and the diphenate. Since the diphenate is not formed with the weak base then it can hardly be expected to follow the same kinetics. Rather than growing a chain from both ends at a time, as in the case of the strong base method, the weak base method requires that the chain grow only on one side at a time. This in itself, along with the insolubility of the base and possible hydrogen bonding of unreacted phenol to phenate are very likely reasons why the reaction is slow in comparison to the strong base method.

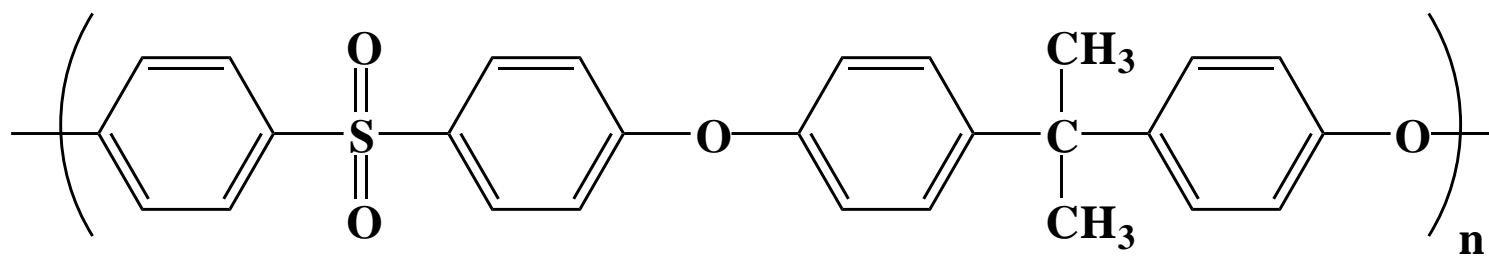
Industrial production requires rapid reaction times in order to maintain low cost and this is the main advantage of the strong base method. The weak base method provides polymers which are equally good however, the slow reaction rate may, in some cases, prohibit its use industrially. The key advantage in the weak base method is that it is more applicable to polymers in which the diphenate is found to be highly insoluble. The monophenate formed by this mechanism may show much greater solubility making this method to be preferred for the facile synthesis of these polymers.

2.3 Physical Characteristics of Poly(arylene ether sulfone)s

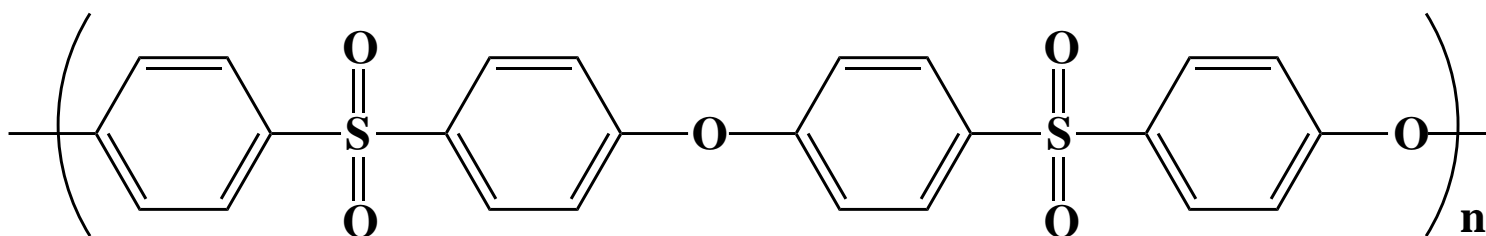
Polysulfones display many properties suitable high temperature engineering applications. They are transparent, stiff (high modulus), tough thermoplastic materials with relatively high glass transition temperatures ranging from 180-250°C, depending on the exact backbone structure. The backbone characteristics that are in common are the rigid phenyl groups connected by flexible ether and inflexible SO₂ linkages. The general rigidity of this class of polymers comes largely from the inflexible structures while the toughness may be associated with the ether linkages which allow for some mobility between rigid segments even below T_g.⁴ These polymers also possess good hydrolytic and thermal oxidative stability, which suggests application where high temperature molding is required. Good electrical properties are also a common feature in this class of materials. Polysulfones can be injection molded, blow molded and extruded under conditions typical of the processing required for other highly viscous amorphous polymers like polycarbonates. High temperatures on the order of 300-400°C and high pressures are necessary to melt process the materials. Polysulfones can also be machined very nicely due to the high glass transition temperature and yet the inherent toughness of the material cuts well without cracking or shattering.⁴⁹

Three commercial polysulfone backbones are shown in figure 2.7. These commercial polymers are all rigid and tough, with high unnotched impact strengths. This toughness is believed to be derived largely from relaxations which are evidenced by a second-order (β) transition at around -100°C . Many dynamic mechanical studies have been carried out on a variety of polyarylene ether sulfone polymers to determine the origin of this low temperature transition.^{10,58} It is generally believed that the low temperature transition is due to more than one mechanism, including rotation or “ring flipping” about the aryl ether bond. It may involve a complex formed with the sulfone moiety with sorbed water. The mechanical loss peaks due to these low temperature motions overlap, making it difficult to distinguish one from the other in most cases.

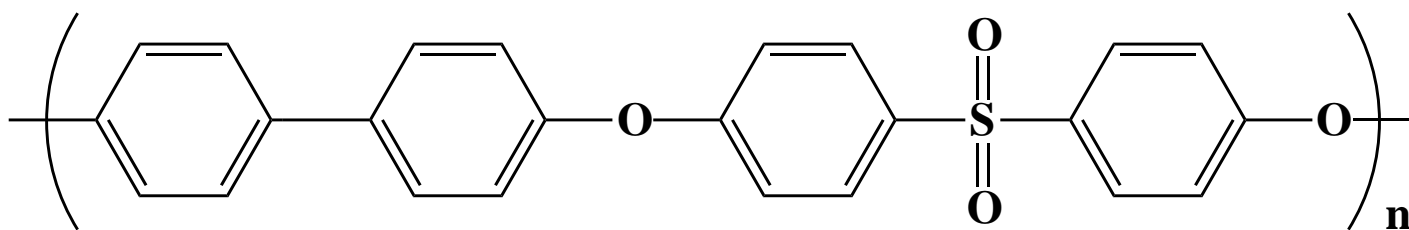
Polyarylene ether sulfones have very good hydrolytic stability compared to other thermoplastic polymers such as polycarbonates, polyesters and polyetherimides.⁵⁹ They show little significant change in mechanical properties after hours of exposure to hot water and steam. The rate of polymer hydrolysis is not affected over a broad range of pH, and they are particularly resistant to aqueous mineral acid, alkali, and salt solutions. Solvent resistance in organic solvents is another matter. Polysulfones will crack, craze and swell even in organic solvents where significant dissolution does not occur, which is typical of amorphous thermoplastic materials. Some polyarylene ether sulfones such as



UDEL bisphenol A polysulfone



Victrex polyethersulfone (PES)



Radel R polyphenylsulfone

Figure 2.7 Commercial Polysulfone Backbones⁴⁹

the polyphenylsulfone (Radel) will crystallize from solvent, sometimes forming unstable solutions.⁶⁰

The many highly desirable properties of polyarylene ether sulfone, as well as the ability to tailor the properties by changing structure, molecular weight, and endgroups among many other variables enables them to be widely used in many applications. Medical and food service applications which require materials to withstand repeated exposure to steam and sterilization procedures are one major market. Bisphenol A polysulfone is the least expensive of the commercial class of materials and therefore is the most widely used.³⁴ Another application is as a gas separation membrane support. Additional electrical uses are a result of the relatively low dielectric constants achievable with polysulfones.

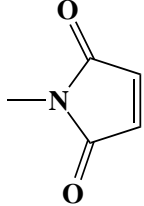
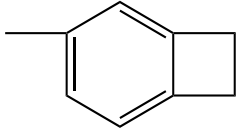
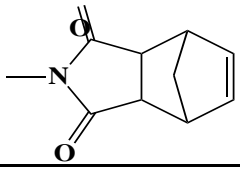
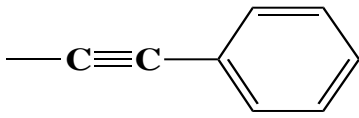
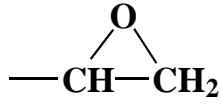
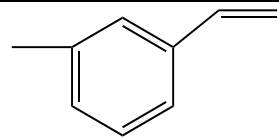
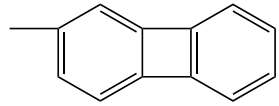
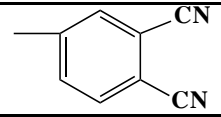
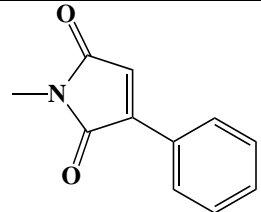
2.4 Thermosetting Poly(arylene ether)s

Polymeric materials are conveniently separated into two distinct classes: thermoplastics and thermosets. Thermoplastics are high molecular weight linear polymers which can usually be either solvent cast or melt processed into a manufactured part. Thermosetting resins are typically initially very low molecular weight polyfunctional species (or at least oligomeric in nature) which incorporate functionality on the chain ends or along the backbone. These groups can further react in a crosslinking reaction either alone or with coreactants to produce an insoluble and infusible network. There are many high performance thermoplastics with characteristics desirable for aerospace structural applications. These include polyimides, polybenzobisthiazoles, polybenzobisoxazoles, aromatic polyamides, polybenzimidazoles, LC-polyesters, polyether ether ketones, polyether sulfones, poly(amide-imides), polyquinolines and polyquinoxalines.⁶¹ While these polymers do possess good high temperature thermal and mechanical properties necessary for aerospace structural applications their other intrinsic properties may be insufficient. Typically, high-performance linear amorphous polymers show poor solubility in organic solvents making processing difficult from solution but will still swell, crack or craze in many organic solvents. This decreases the long term performance of the material in a structural application. Processability is another major drawback of many thermoplastics. Extremely

high melting points and high melt viscosities make melt processing difficult as well. Melt viscosity is a function of molecular weight so there can be some amount of trade off in that area. Lowering the molecular weight of the thermoplastic just enough to improve processability without sacrificing too much in thermal or mechanical properties is one compromise that can be made. An alternate better solution is to reduce the molecular weight drastically to improve processability and to incorporate reactive functionalities on the molecule, which can further react into a crosslinked thermoset. The thermosetting resin can be tailored through structure, functionality and molecular weight to possess many useful properties designed to fit a specific application.

Some well known reactive functionalities are shown in table 2.1. Many of these structures have been used to endcap oligomers which are then thermally cured to crosslinked structures independently, or via catalysts or coreactants. It is clearly important for structural thermosets that the curing reaction of the functionality produce no volatiles. Void free structures are necessary to maintain good long term durability and mechanical integrity. This requirement makes the use of some of the functionalities in table 2.1 impractical. Another requirement for most structural components is impact strength or fracture toughness. The structures formed in the crosslinking reaction can also have an affect on the

Table 2.1 Reactive Groups for High-Performance Thermosets⁶¹

Functionality Structure	Functionality Name	Approximate Cure Temp. (°C)
	maleimide	200
—OCN	cyanate ester	170
	benzocyclobutene	200
—C≡CH	ethynyl	200
	nadimide	300
	phenylethynyl	350
	epoxide	variable with catalyst and co-reactant
	styrenyl	200
	biphenylene	300
	phthalonitrile	250
	phenylmaleimide ⁶²	350

properties of the thermoset by adding rigid ring structures to the material on curing. This can be advantageous when thermal properties are considered by increasing thermo-oxidative stability and increasing T_g but can have a detrimental effect on the toughness of the resulting structure, usually as a result of it being associated with increased network density.

Processability is an important feature in the design of thermosetting resins. In order for a resin to be processed into a composite or molded part it must flow before the gel point occurs. A certain minimum temperature must be reached in order for a material to flow, which requires an amorphous oligomer to be well above its glass transition temperature and a semi-crystalline oligomer to be above its melting temperature. The difference between this minimum flow temperature and the temperature at which the curing reaction takes place at a reasonably rapid rate is known as the processing window. Crosslinking functionalities such as shown in table 2.1 react at different temperatures and have different mechanisms of cure, which in turn provide linking structures which impart different properties into a thermoset. The nature of the backbone structures also influences properties, so these are two variables to be considered when choosing a thermosetting resin for a specific application. Once a backbone and functionality have been chosen, then the processing window must be investigated. Molecular weight of the resin or oligomer can have a large effect on the processability of

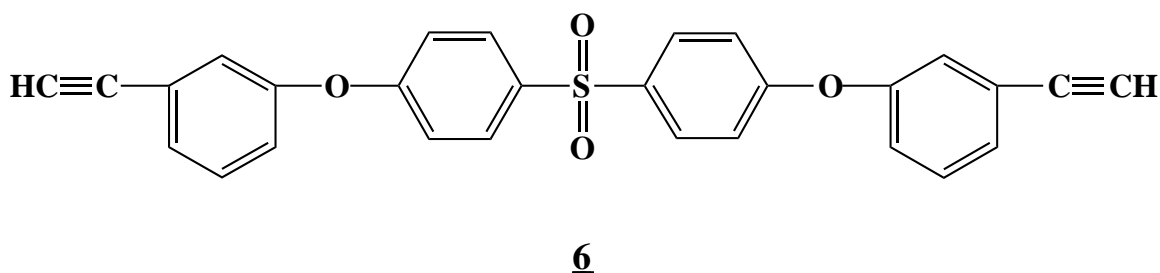
the material because the melt viscosity scales with the 3.4 power of weight average molecular weight. Higher molecular weights have higher flow temperatures and higher viscosities which can reduce the processing window. Molecular weight of the starting material also has an effect on the properties of the cured thermoset. A thermoset derived from a very low molecular weight resin can have a higher crosslink density, which will usually provide a higher glass transition temperature but will also most often show poorer mechanical properties. These are just some examples of the critical parameters of thermosetting networks which allows for the design of materials for specific applications.

2.4.1 Poly(arylene ether sulfone) Thermosets

Thermosets derived solely from functionalized poly(arylene ether sulfone) oligomers are the subject of this research. In the quest for high performance materials suitable for aerospace structural applications involving both adhesives and polymer matrix/carbon fiber composites, different arylene ether sulfone backbones and thermosetting endgroups have been investigated.^{12,13,15-18,28,29,61,63-85} A large portion of the research since the early 1980s and continuing to the present time has been in the area of acetylene terminated sulfone resins known as ATS resins. In the late 80s and early 90s research groups began

to develop an interest in alternate endgroups to achieve more desirable properties from the cured sulfone materials.

In 1980 Hergenrother⁶⁷ reviewed acetylene containing precursor polymers which included a section on sulfones. He reported that different acetylene terminated ether sulfone containing materials were under investigation for their potential use as composite matrices and/or adhesives. One such material was **6**. **6** had been previously used in an attempt to increase the processability of highly viscous thermoplastic polysulfones by blending it with the reactive



plasticizer. The preliminary evaluation of **6** as a matrix material involved thermal curing at 177°C, followed by a post cure at 260°C for 16 hours. The post cure step was not uncommon in the this class of materials because often the T_g of the thermoset would reach that of the lower cure temperature, vitrify and inhibit further curing. Flexural and interlaminar shear strengths were reported for a unidirectional composite prepared from **6**. It was also reported in this

review that work was being undertaken by several groups to attempt to elucidate the cure chemistry of the acetylene group, but that the seeming complexity of the thermal curing mechanism made identification of the cured compounds exceedingly difficult. Hergenrother concluded that the ethynyl substituted sulfone oligomers had many attractive properties for adhesive and composite matrix applications but that there was much work to be done in order to optimize the materials for future use.

Hergenrother²⁹ reported the synthesis and characterization of ethynyl terminated polysulfones based on the commercial UDEL backbone (**1**). A series of oligomers was synthesized with molecular weights ranging from 3,000 to 26,000 g/mole. The materials were cured at various temperatures ranging from 250-300°C and relevant properties of the cured materials were evaluated. Solvent resistance of the materials was good, although swelling of the cured thermosets occurred in chloroform. Glass transition temperatures of the cured polymers were as much as 12°C above that of the thermoplastic UDEL[®] and increased with lower molecular weight of the precursor materials as expected. Molding of the materials was found to be difficult, especially with the lower molecular weight oligomers. The difficulty arose from the fast reaction of the ethynyl groups at the molding/curing temperature. All of the materials were molded at 316°C. This high temperature was probably unnecessary at least for

the lower molecular weight oligomers which had uncured T_g s in the 160-180°C range and may have made the problem worse. Molding of these materials is very difficult because the onset of cure begins at around 130°C, which is even below the T_g of the oligomers. Therefore, whatever temperature is chosen for good flow properties will be in the range of curing temperatures and the material will begin to cure as soon as it flows. It was hoped that the viscosity of the material would be so low at high temperature that it would consolidate before gelation occurred. Unfortunately, the higher temperature increased reaction rates and for the lower molecular weight oligomers with the greater number of endgroups, gelation competed with the flow of the material, resulting in poor consolidation. The thermal stability of the cured polysulfone networks was found to compare unfavorably to the thermoplastic UDEL in air but the degradation behavior of the two in nitrogen was indistinguishable. The structures formed during the curing reaction were not identified but this seemed to indicate that they were more susceptible to oxidative degradation than the polysulfone backbone.

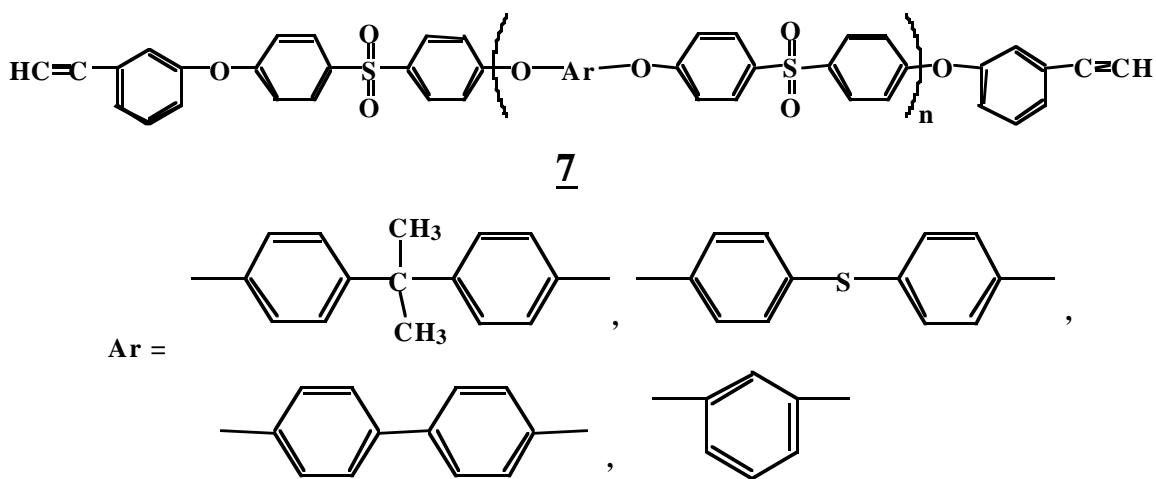
It had been determined that the properties of the thermosets largely depended on the cure conditions of the ATS resins.^{72,74,75} In 1983, workers in the Air Force Wright Aeronautical Materials Laboratories presented research which investigated the kinetics of the acetylene terminated resins cured in nitrogen and air atmospheres and its effects on the mechanical properties of the

thermosets.^{66,73} Their experiments were based on the curing of a material based on **6**. Their resin was about 77% **6** with a mixture of 0,2 and 3 repeat units of the diethersulfone unit. They were interested in discovering what the effect of vitrification had on subsequent curing of the resin. Curing was conducted in nitrogen at 130°C and only progressed to 72% conversion even after 89 hours. The cure was halted at this temperature due to the inability of the endgroups to react in the vitrified state. Compilation of data and some calculations led these researchers to claim that the T_g s of these incompletely cured materials were higher than the cure temperature, indicating that the curing reaction was carried out in the glassy state to some extent. A better explanation would allow that the exothermic enthalpy increased the actual reaction temperature.

The Air Force scientists were also interested in the effect of the atmosphere on the cure of ethynyl terminated sulfone resins. They determined that there was a difference in the materials produced by curing in air vs. nitrogen. The air cured resin produced a thermoset with a moderately lower T_g ($T_g = 370^\circ\text{C}$) than the nitrogen cured material ($T_g = 390^\circ$). The rate of cure was also slower in air. They proposed the possibility that the oxygen inhibited the radical initiated chain propagation step. The researchers also noted that the thermosets underwent oxidative crosslinking after heat treatments at 380°C in air. However, they did

not compare this to a thermoplastic analog, so it was unclear if this result was an effect of the crosslinks or due to reaction on the polymer backbone.

In 1985 other workers⁸⁵ at the Wright-Patterson Air Force Base laboratories reported the synthesis of higher molecular weight sulfone resins than **6**, but not polymeric as reported by Hergenrother^{29,68}. A representative of the general structure, **7**, is shown below. These structures were chosen to enhance the toughness of the thermoset but still retain good processability. The synthesis of these structures used methods developed to offset the stoichiometry



by 4:1 to produce oligomer/monomer mixtures of fluorine terminated products, the monomer structure where $n = 1$. The monomer could be separated from the oligomeric mixture through column chromatography and the oligomer/monomer

ratio varied with the bisphenol used. It was necessary to use the 4,4'-difluorodiphenylsulfone vs. the chlorinated version of the monomer because the subsequent endcapping with the cleavable endcapping agent needed to be carried out at lower temperatures than that necessary for reaction of the less activated chlorinated site. The final step in the synthesis involved cleavage of a acetone protecting group to produce the acetylene terminated resin. This method of synthesis was an improvement over previously used methods because the palladium catalyzed step to produce the reactive endgroup took place before the addition to the oligomer structure. The palladium catalyzed reaction had been observed to leave entrapped metals in the reactive resins when carried out in situ. This new method allowed removal of the bulk of the before the addition to the oligomer took place, serving to produce a more stable material, since the metal could cause crosslinking to occur at very low temperatures.

Curing of monomers and monomer/oligomer mixtures was studied at 288°C in air for 8 hours. It was of interest to determine what the effect of different amounts of the oligomers would have on the thermomechanical properties. All of the monomers and monomer/oligomer mixtures had initial T_g s in the range of 40-55°C, which the authors found to be too high for good processability with the current methods. The 4,4'-biphenol system possessed a high T_m and provided no processing window at all. The T_g s of the cured

materials were 230-370°C for the sulfur and resorcinol based resins making them the most likely candidates for further study. The bisphenol A based resin had a T_g on the order of the thermoplastic UDEL[®] ($T_g = 190^\circ\text{C}$) for the monomer and even lower for the oligomeric mixture, making it unsuitable for aerospace applications. The T_g values obtained for the bisphenol A based system are lower than would have been expected based on the data obtained on similar materials by Hergenrother^{29,68} indicating that there may have been some unidentified problem with this particular material. Thermal stability of the cured resins was evaluated by air aging at 315°C for 200 hours. Weight losses on the order of 20-40% were found which the authors considered “good thermal stability”. The general conclusions based on this work was that a better synthetic route had been found to acetylene terminated sulfone resins and that some promising backbone structures had been investigated, but that the processability of the materials still needed work and an investigation into reactive diluents would be following after scale up of the synthetic method had been accomplished.

Despite the findings of the previous workers at the Wright Patterson labs⁸⁵ and researchers elsewhere^{28,76}, in 1991 associated researchers contracted a large pilot plant batch of the ATS used in the 1983 studies^{66,73} to be made by the original procedure. Apparently, the somewhat more difficult to process materials which had been produced by alternate methods of endcapping were not

of interest for large scale procedures. The synthesis of this ATS resin involved the direct palladium catalyzed coupling of the protected acetylene on the preformed resin, followed by deprotection to produce the mixture of acetylene terminated products. The mixture, although more complex than a monomeric species, was found to be more easily processed due to suppressed crystallization, producing lower viscosity. A large research effort to characterize this ATS resin for use in structural aerospace applications followed.^{82,83} The first effort provided detailed chemical characterization of the uncured resin.⁸² The ATS resin mixture was first fractionated by column chromatography and each fraction was analyzed. Elemental analysis was used to identify the ratios of elements present in each fraction. Palladium was found to constitute about 30 ppm of the resin mixture and some separated fractions were found to have very high levels (up to about 800 ppm). The fractions with the very high levels of palladium contamination had structures which could chelate the metal because it was believed that the metal should have been removed through the purification, which consisted of repeated passage through silica gel. Palladium metal is capable of catalyzing crosslinking at very low temperature. Through subsequent analysis of the resin mixture the researchers were able to identify many other impurities arising from side reactions during the multi-step synthesis of the resin. Most of these side reactions were attributed to the presence of small amounts of

contaminants in the original reagents. It was concluded that this was a complex mixture, but typical of what would be available from commercial sources.

The second thrust of this same research effort was to characterize the thermal properties of the ATS resin.⁸³ Glass transition temperatures were measured for the ATS mixture as well as for each of the separated fractions. The monomer was the only pure material with a desired room temperature “tack and drape”. In other words it was the only pure material with a T_g well below room temperature. The only acceptable prepregging technique of the time involved the flow of the resin at room temperature. The resin mixture was also a tacky liquid at room temperature probably because it was a mixture and because it was largely made up of the monomeric species. The onset of cure and the maximum of the curing exotherm were measured by DSC at different heating rates. It was found that the onset of cure was inversely proportional to the size of the resin species. The resin mixture was found to have a cure onset 40°C lower than the pure monomeric species. The rate maxima were all very close, so the actual range of cure temperature was broadened by the larger species. The T_g s were measured for each of the cured materials and it was found (as should be expected) that the T_g of the thermoset increased with decreasing size of the starting resin, showing a dependency on the crosslink density. The T_g of the resin mixture was not measurable by DSC as is sometimes the case with a very highly crosslinked

structure. The fully cured monomer had a T_g of 328°C and previous studies by other methods indicated that the T_g of the fully cured resin mixture was on the order of 370°C⁷³. Obviously some reactions were occurring in the mixture which were not present in the reactions of the separated species.

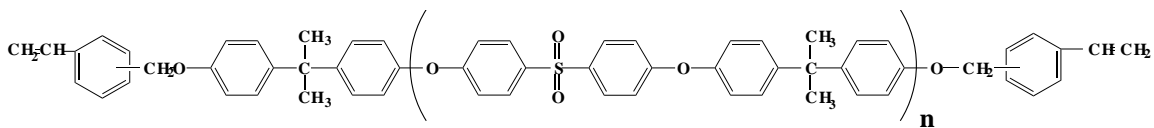
These researchers also investigated the thermal stability of the cured resins under different conditions by thermal gravimetric analysis and through analysis of trapped degradation products. They concluded that the thermal stability of the cured resin increased with increasing crosslink density and/or polyene concentration. Thermal instability in the temperature range of 316°C or 600°F was found to be oxidative in nature but was not found to change with crosslink density. Isolation of early degradation products indicated that the sulfone linkage was the thermally unstable linkage rather than the crosslink or polyene structures. Thermal instability over 400°C indicated that this was too high a temperature at which to post cure the cured resin, but there was also some indication that prolonged post cures at substantially lower temperatures under conditions which would minimize weight loss due to degradation could serve to increase the T_g . Whether the increase in T_g would be due to further crosslinking by the original mechanism or degradative crosslinking was not discussed in detail.

The low viscosity of the uncured ATS resins and the high solvent resistance and glass transition temperatures of the cured ATS resins provide good

properties of aerospace structural applications but the materials are inherently brittle due to the high crosslink densities which must be attained to achieve the beneficial properties. Research has been carried out in the area of semi-interpenetrating networks based on ATS resins. In 1993 researchers in China reported the investigation of the use of a blend of an ATS resin, similar to **6** but with all para linkages, with different polysulfone thermoplastics. The purpose of this investigation was to identify if the combination of these two materials could both improve the toughness of the cured material and enhance the processability of the thermoplastic.^{80,81} They reported that the uncured resin produced compatible blends with both bisphenol A polysulfone and a polysulfone based on phenolphthalein as the bisphenol. The thermoplastic did not appear to interfere with the curing reaction but as the cure took place so did phase separation of the blend. This phase separated material possessed two T_g s, the lower one for the thermoplastic phase and the higher one for the thermoset phase. The cure temperature used was found to affect the morphology of the phase separated structure. Curing at temperatures of 270-300°C produced a fully incompatible co-continuous structure. Temperatures greater than 300°C produced a co-continuous structure which evidently was more compatible because the T_g of the thermoplastic phase was found to be increased over that of the pure thermoplastic. This result is presumably due to the rapid rate of cure at this

temperature trapping thermoplastic into the network structure phase separation. Solvent resistance and mechanical properties were not reported for these phase separated systems.

ATS resins are by far the most prevalent curable arylene ether sulfone materials in the literature but there are other endgroups that have been investigated and a few will be mentioned here. Percec and coworkers presented a comparison of the properties of their styrene terminated sulfone resins, **8**, with ATS resins in 1987.⁶⁵ The styrene terminated oligomers were based on bisphenol A polysulfone and a series of molecular weights were synthesized

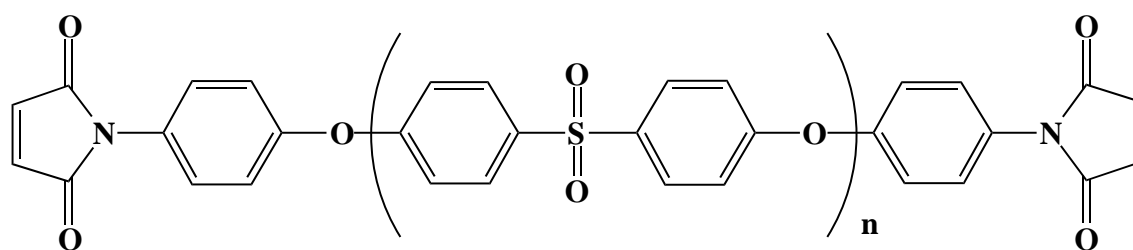


8

ranging from the monomeric molecular weight of 970 to about 6,700 g/mole. The cured glass transition temperatures ranged from 180-195°C, after curing at 200°C for 16 hours, and were slightly dependent on the initial molecular weight of the uncured material. These temperatures are slightly lower than the reported T_g values²⁹ for identical backbone ATS oligomers. This T_g range is also on the order of the T_g of the thermoplastic UDEL which also possesses the same

backbone structure. TGA results indicated that the cured materials showed similar degradative behavior in air and nitrogen and that the thermal stability of the thermosets was lower than the thermoplastic. They observed a trend where the degradation occurred earlier in the samples which were initially lower in molecular weight and concluded that this was due to the methylene ether bond being the weak link. The authors compared their resin to a low molecular weight ATS, **6**. As was previously mentioned a better comparison would have been to the ethynyl terminated sulfone resins reported by Hergenrother.²⁹ It was concluded that the T_g was significantly lower due to the difference in molecular weights and therefore crosslink density of the materials and related to a great deal of scatter in the literature data on the ATS resin. It was only possible to say that there were “significant similarities as well as differences”.

Yee et.al. presented a comparison of maleimide terminated polysulfones with ATS oligomers in 1991.^{70,71} The structure of the bismaleimide polysulfone synthesized for this research, **9**, is based on a backbone structure similar to **6**. A series of molecular weights was synthesized ranging from 1,000-3,000 g/mole. Ethynyl terminated bisphenol A polysulfones were also

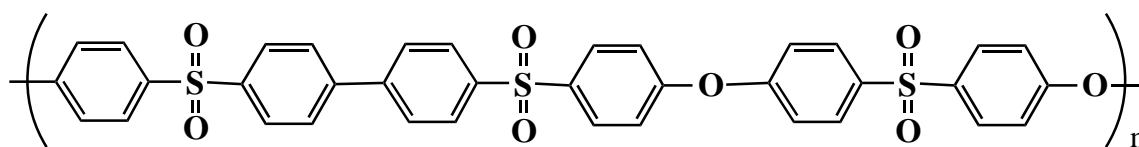


9

synthesized in varying molecular weights from 2,600-12,000 g/mole in collaboration with researchers at NASA Langley Research Center.²⁹ Solvent cast films were dried on glass plates in stages to first remove the volatiles and then cure the oligomers. The very low molecular weight maleimide oligomers formed very brittle cured films. The cure cycle for the acetylene and maleimide oligomer was the same: 50°C/4 hours, 150, 170, 210°C/1 hour each, 250°C/4 hours, except that the maleimide resins needed a post cure of 280°C/1 hour in nitrogen. DSC results from the uncured oligomers indicated that there was little if any processing window available for these resins, since the T_g s or T_m s occurred immediately before the onset of cure shown by the cure exotherm. The maleimide resins cured to brittle films for the most part while the ethynyl terminated resins produced foldable films. This distinction could be related to the crosslinking mechanism or be due in large part to the generally higher molecular weights of the ethynyl terminated resins before cure. The T_g values of the cured materials reflect a similar trend in that the lower molecular weight

maleimide terminated resins cure to T_g values in the range of 250-270°C and the ethynyl terminated resins to T_g values of 210-225°C. Again, this could be due to crosslinking differences or largely attributed to molecular weight and backbone structure differences. The ductility of glassy polysulfone thermoplastics is related to the β relaxation at around -100°C. The β relaxation peaks were identified for many of the cured resins by dynamic mechanical analysis and dielectric analysis. The dielectric loss data showed that the β peak shifted to higher temperatures as the crosslink density increased for each resin system. The maleimide terminated resins also showed a greater shift overall than the ethynyl terminated resins, suggesting that the crosslink density was greater in the maleimide system. Once again, the difference in backbone structure and initial molecular weight make these comparisons tenuous.

Researchers in Belgium supported by ICI Materials in England synthesized, characterized and reported a new series of maleimide terminated poly(arylene ether sulfone) oligomers.^{78,79} The backbone structure used for their research, **10**, was synthesized from bisphenol S and a long chain dichloride using the potassium carbonate based nucleophilic aromatic substitution reaction. The stoichiometry was offset to produce chlorine terminated oligomers of



10

molecular weights ranging from 3,700-11,700. These oligomers were subsequently endcapped with m-aminophenol under conditions similar to the polymerization conditions to produce amine endgroups which could be reacted further with maleic anhydride to form the maleimide terminated polysulfones. The apparent insolubility of the monomers used and the polymer formed required diphenylsulfone as the solvent for their polymerization reaction at 285°C. The necessity of using such a high temperature for the synthetic step may have contributed to the results of the synthesis. They found that the chlorine terminated polymers had undergone ether interchange during the reaction and this had resulted in the presence of some phenolic terminations in the polysulfone as well. These oligomers were further reacted in the intended steps anyway to form partially maleimide endcapped oligomers. The phenolic endgroups reacted with acetic acid formed during the generation of the maleimide endgroups to provide protected acetate endgroups. The curing and properties of three oligomers of this series were studied. In addition a completely amine terminated poly(ether sulfone) copolymer was synthesized in which the ratio of ether to

sulfone linkages was 10:7 and a $M_n = 10,800$ by GPC. After repeated fractionation of this copolymer a series of 8 amine terminated fractions were separated and endcapped with maleic anhydride to provide maleimide terminated oligomers with M_n s ranging from 2,100-28,700 g/mole as determined by NMR. The high temperature polymers which were not fully endcapped with maleimide endgroups were cured at three different temperatures, 250, 280, and 300°C, for one hour. T_g s were measured on the cured samples as a function of time at each temperature and the percentage of insolubles was measured to compare the change in the glass transition temperature with conversion. None of the high temperature polymers reached 100% gel fractions even when cured at 320°C. This is likely due to the incomplete endcapping of the material, as the highest gel fractions reached were on the order of 80% for these systems. Vitrification also played a part in stopping the cure reaction at 250°C. The highest T_g reached for the lowest molecular weight system cured at 300°C was around 270°C. This T_g was also attained by the higher molecular weight high temperature oligomer at the higher cure temperatures and in both cases the gel fractions were about 80%. It is difficult to draw conclusions from the data due to the incomplete endcapping of the materials and the fact that the three different molecular weights were incompletely endcapped to differing extents.

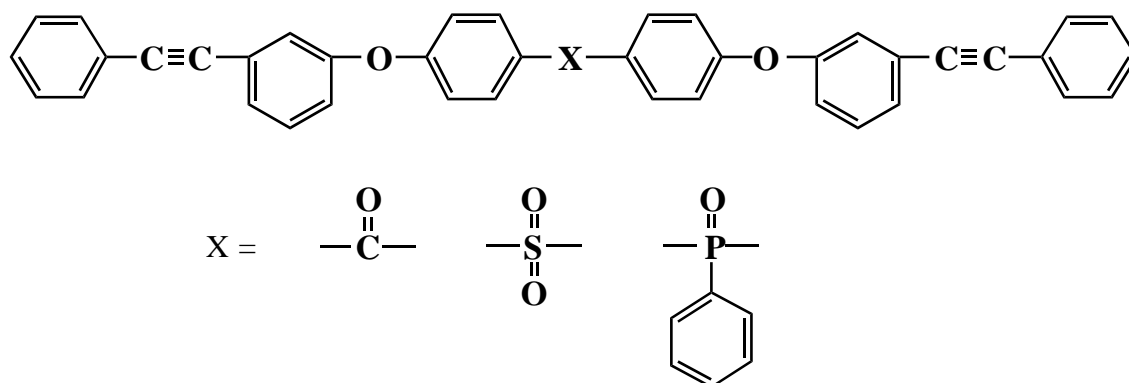
The fully capped copolymer fractions were cured for 16 hours at 260°C to achieve full crosslinking. All of the T_g s were about the same and the gel fractions were 93-97%. The authors concluded from their study that the change in T_g arose from the inherent rigidity of the backbone combined with the number of chain ends. Their assertion was that the curing oligomer acted as a blend of higher T_g entangled polymer with lower T_g dangling ends, as the number of ends decreased the T_g increased. When the molar mass was initially high the effect was less noticeable due to the low concentration of endgroups. This means that the increase in T_g with crosslinking time is directly related to the decrease in chain ends.

Recently⁸⁶, a great deal of interest has been directed towards phenylethynyl terminated resins and oligomers as a improvement over the original ATS systems. Much of the research on the phenylethynyl moiety has utilized polyimides, but limited effort has also been applied to phenylethynyl terminated poly(arylene ether sulfone) oligomers and resins. Thus researchers at NASA Langley Research Center developed methods for the synthesis of phenylethynyl terminated poly(arylene ether ketone)s and reported these in 1993.^{63,69} Various bisphenols and ketone activated dihalides were used in conjunction with 4-fluoro-4'-phenylethynylbenzophenone as the endcapper to synthesize controlled molecular weight phenylethynyl terminated polymers. The

synthesis utilized potassium carbonate in dimethylacetamide using toluene as the azeotroping agent. Each backbone structure was synthesized in two different molecular weights, 3,000 and 6,000 g/mole, which were cured at 350°C for one hour. Single lap shear adhesion measurements were conducted and the values were about 2,000-4,000 psi for all of the systems, with the higher molecular weight oligomers producing the better values, as expected. The T_g values obtained for these cured polymers were odd in the sense that the higher molecular weight oligomers provided higher T_g s than the lower molecular weights in all cases, by as much as 20-30°C. Substantial increases in the T_g s of both molecular weights occurred on curing. This may indicate the lower molecular weight oligomers at least were not fully cured. Measurements of the gel fraction or elastic modulus above T_g were not reported so it is impossible to evaluate incomplete cure as a possibility. It was reported that the cured films were brittle and the lap shear values reported are low compared to phenylethynyl terminated polyimides. These are indications that perhaps the curing temperature and time used for their experiments were insufficient to obtain high gel fractions and therefore good mechanical properties in the cured films.

McGrath and coworkers reported the synthesis and characterization of a series of phenylethynyl terminated arylene ether resins in 1995.¹³ 3-Phenylethynylphenol was used to incorporate the phenylethynyl moiety into low

molecular weight resins of the structure **11**. The resins were shown to possess low softening temperatures of 50-100°C. The cure reaction of the phenylethynyl group is substantially higher (150°C) than the corresponding ethynyl group and this allowed for a greatly increased processing window.



11

The comparison with the ATS resin is obvious in that the structures of the sulfone are almost identical except for the phenyl vs. hydrogen substitution on the terminal ethynyl carbon. Curing of the ATS resin occurs at temperatures as low as 130°C, but due to vitrification as the T_g of the curing resin increased it was necessary to cure at much higher temperatures to reach a high gel fraction. The high temperature relative to cure exotherm causes the reaction to proceed at a very rapid rate making processing more difficult. The highly crosslinked T_g values for the ATS resins can be on the order of 360°C after a post cure step.

The phenylethynyl (PE) resin does not begin to rapidly cure until temperatures of about 350°C. This allows ample processing time and a great deal of flexibility. It is also of interest that even though the structures of the backbones are almost identical, the T_g of the highly crosslinked PE resin is 100°C lower than that of the ATS resin. This indicates a substantial difference in the mechanism of cure as well which may include chain extension to increase the crosslink density and thereby reduce the T_g of the cured material.

Further characterization of the phenylethynyl sulfone resin and an alternate synthetic method were reported in 1996.^{15,84} The sulfone resin was synthesized using the strong base method which in principle is important for industrial usefulness, because a more rapid reaction rate equates to a more economical process. The difficulty and expense of the synthesis of the endcapping agent is the key economic feature for the industrial synthesis of this material. Thermal analysis showed that the resin's cure was complete after a cure cycle of 370°C for 60 min and a broad T_g was observed between 270-280°C for this highly cured material. The resin was compared to poly(arylene ether sulfone) oligomers terminated with phenylethynyl groups and it was concluded that the resin cured to a high gel fraction much faster than the oligomers and that the crosslink density was much higher. The higher crosslink density resulted in substantially higher glass transition temperatures and lower adhesive strengths as measured by single

lap shear tests. The synthesis and characterization of the phenylethynyl terminated poly(arylene ether sulfone)s in this study in addition to many others is the subject of this dissertation.

2.5 Network Formation Based on the Curing Reaction of the Phenylethynyl Moiety

Incorporation of the phenylethynyl moiety either terminally or pendant along the backbone of high performance polymers is an excellent method for preparing easily processable network precursor materials. Polymers functionalized with phenylethynyl groups include poly(phenylquinoxalines)⁸⁷⁻⁹⁷, polyamides⁹⁸⁻¹⁰¹, poly(arylene ether)s^{12,13,15-19,63,69,84,102-106}, polybenzoxazoles¹⁰⁷ and polyimides^{5,11,14,61,104,108-119}.

The majority of the recent work has focused on phenylethynyl terminated polyimides. The original endcapper used most for this purpose was 3-phenylethynylaniline, which was reported by Harris and coworkers in 1984.¹⁰⁸ Use of this material and its many derivatives as endcapping agents provided large cure exotherms in the temperature range of 350-420°C, allowing for a large processing window for the high temperature polyimides. More recently the endcapper used most for the synthesis of polyimides has been 4-phenylethynylphthalic anhydride and its analogs which appear to impart similar but not necessarily identical curing properties to the phenylethynyl terminated oligomers and resins.

It is clearly important to elucidate the cure mechanism of the phenylethynyl moiety. Detailed information about the mechanism would provide design

parameters for the synthesis of phenylethynyl polymers for uses in specific applications. Polymers and resins which contain either pendant and/or terminal phenylethynyl groups cure to highly insoluble thermosets. The thermoset is always difficult to characterize, to determine the molecular structure of the crosslinks. Many researchers interested in studying the cure mechanism of the phenylethynyl moiety have used monosubstituted model compounds of low initial molecular weight. These materials undergo thermally induced reactions similar to that of the polymers to produce largely soluble products which are much more easily characterized by chromatography and spectroscopy.^{110,114,120-124}

It is important to note that the cure mechanism which low molecular weight model compounds are found to follow does not necessarily hold true for the oligomer structures. There are two factors which set the model compounds apart from the oligomers in terms of reactivity. Firstly, the relative concentration of reactive groups is different and secondly, reduced mobility of multifunctionalized oligomeric structures would be expected. After one chain end is reacted, the mobility of the second one is decreased to a certain extent, which may be dependent on the molecular weight and structure of the oligomer and/or the level of vitrification achieved in the molten curing polymer. These are important considerations when applying information obtained from model compound studies of the thermal polymerization reaction of phenylethynyl

monomers to multifunctionalized oligomers. Nevertheless, the model compound studies are compelling and interesting.

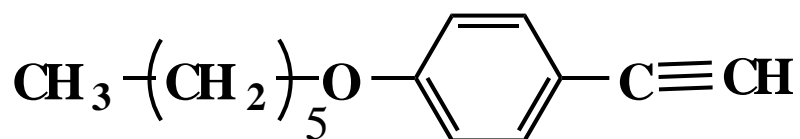
Some studies have been carried out in attempts to systematically characterize the cure of phenylethynyl terminated oligomers by collecting data on cured materials with slight variations in structure and/or through the use of different curing environments.^{19,112,114,118,125}

2.5.1 Investigations of Phenylethynyl Model Compounds

The mechanism of the cure of the ethynyl terminated materials has been studied for a longer time than for the phenylethynyl group. There is obviously a large difference in the curing of the ethynyl vs. the phenylethynyl as judged by the difference in the exotherm temperature. The steric factor of the pendant phenyl group presents a tremendous structural difference as well. Although there are differences, there are likely to be some similarities as well due to the common carbon-carbon triple bond. While the ethynyl group is not the subject of this investigation, a recent publication on the subject will be discussed here because of its relevance.

Sillion, Mercier and coworkers have recently published a study on the thermal polymerization of a monofunctional arylacetylene model compound.¹²⁶

The objectives of the study were to thermally cure and characterize 4-(hexyloxy)phenylacetylene, **12**, to determine the nature and the



12

proportion of the polymerization products. Also of interest, was the effect of the polymerization temperature on the molecular weight and the molecular distribution of the polymer.

A short review of relevant literature^{72,75,127-133} was presented to clarify the knowledge base. The polymerization of the ethynyl moiety takes place at temperatures at or above 130°C without the use of catalysts. The properties of the resulting networks are dependent on many factors such as; structure of the main component and curing conditions. The polymerization involves free radical intermediates. The acetylene functionality disappears more rapidly than the radical species which are produced. Benzene-like trimers have been isolated from monofunctional compounds and they are possibly formed by elimination from growing chains. Polymeric fractions have been isolated and it has been postulated that the polymerization is through a biradical mechanism and that the

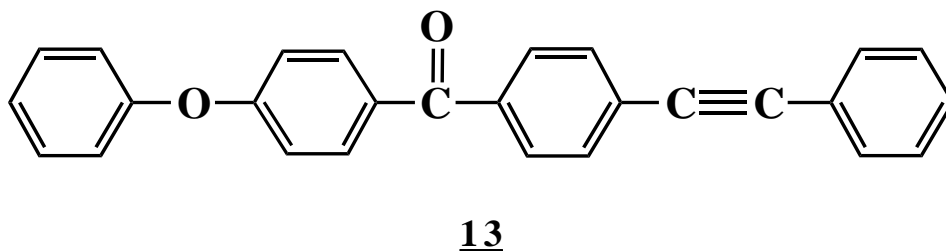
products are polyenic. There have been many investigations into the curing mechanism of the ethynyl group and much information has been gathered, but the real definitive answer seems to be that it is a very complicated mechanism which may take more than one pathway.

The curing of **12** had an onset of cure at 160-170°C and a cure maximum of 240-250°C by DSC. Two isothermal temperatures were used to cure **12**, 180 and 280°C. Also a stepwise cure was used: 180°C/3hr, 220°C/2hr, and 280°C/2hr. Naphthalenic and benzenic structures were isolated from oligomeric species after the curing reactions. The relative amounts of the cyclics did not vary significantly with cure cycle and neither did the ratio of cyclics to oligomers (30/70). Comparisons to other studies led to a conclusion that the ratio of cyclics to oligomers did not change with changing structure of the substituents on the model compound, but the relative ratios of the cyclics to each other was affected. The size of the oligomers was affected by the temperature of cure as judged by SEC. Increasing the temperature and time of the polymerization caused oligomers which had formed initially to depolymerize and the SEC peak to shift to higher elution volumes.

The information obtained on the ethynyl model compounds does not necessarily directly relate to the phenylethynyl compounds but it is likely that there are similarities. It is unlikely that the cyclization reaction is present or at

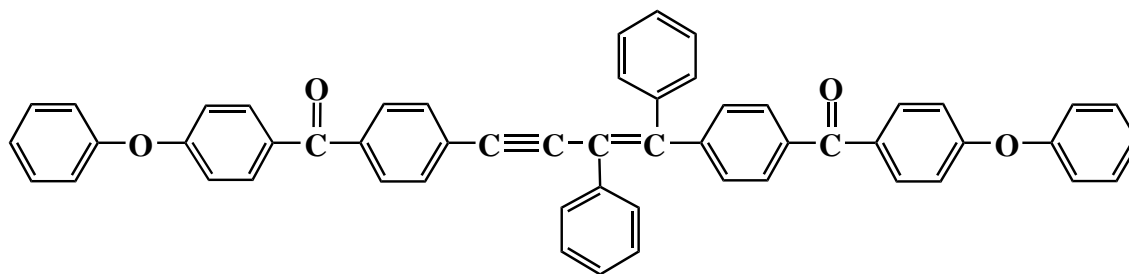
least as prevalent in the phenylethynyl compounds due to the increased steric hindrance of the terminal phenyl group. It is possible that the polymerization mechanism which has been proposed to form a polyenic backbone is similar and present to a larger extent than in the ethynyl compounds.

Two very recent publications propose possible mechanisms of cure in phenylethynyl model compounds.^{120,122} Wood¹²² has investigated the cured products of **13** using DSC, diffuse reflectance FTIR, ¹³C NMR and LC-MS.

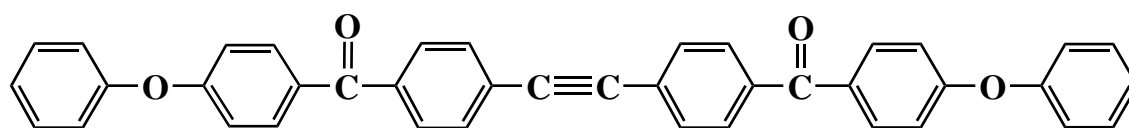


This model compound is based on the phenylethynyl endcapper, 4-fluoro-4'-phenylethynylbenzophenone which has been used in the synthesis of phenylethynyl terminated poly(arylene ether)s.^{63,69} A number of dimers, trimers and tetramers were isolated from higher order products. There was evidence of different dimer structures being present by mass spectroscopy. Three proposed structures which fit some of the peaks in the mass spectra for the isolated materials are obtained by three different proposed mechanism. One

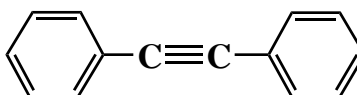
proposed mechanism involves the tail to tail addition of the phenylethynyl groups and a subsequent phenyl migration to form **14**. The second proposed mechanism involves the formation of a cyclobutadiene resulting in a rearrangement to produce two fragments, **15a** and **15b**. The third proposed mechanism is the reaction of the phenylethynyl group with a terminal phenoxy group, also involving a phenyl migration step, to provide **16**. Peaks were found



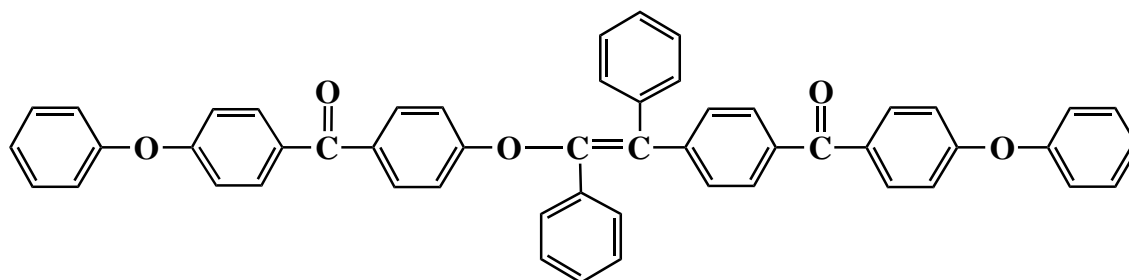
14



15a



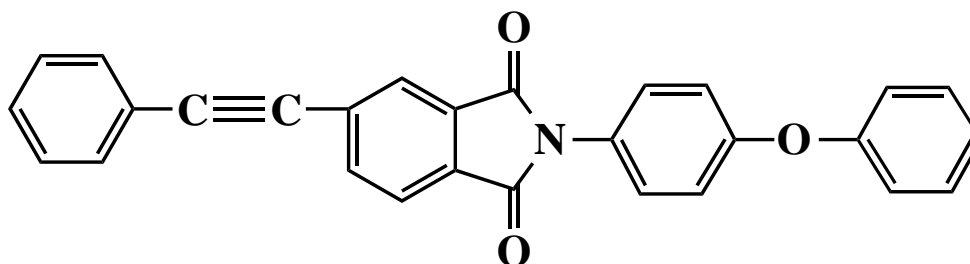
15b



16

in the mass spectral data which are unique as well as common to the formation of all of these structures. These researchers anticipate further evidence involving ESR to establish the presence of stable radicals during the cure in their continuing effort to investigate this complicated curing mechanism.

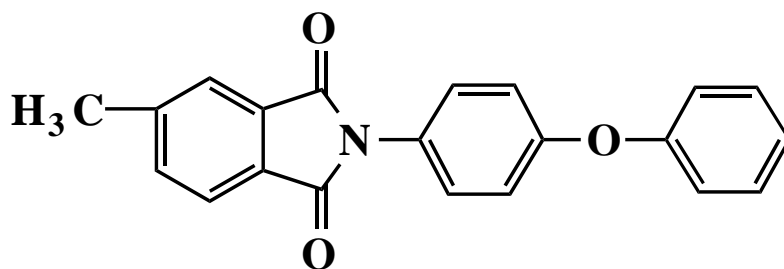
Holland and McGrath¹²⁰ are currently investigating the curing of another model compound, **17**, based on the phenylethynyl endcapper, 4-phenylethynylphthalic anhydride. This endcapper is commonly used to synthesize



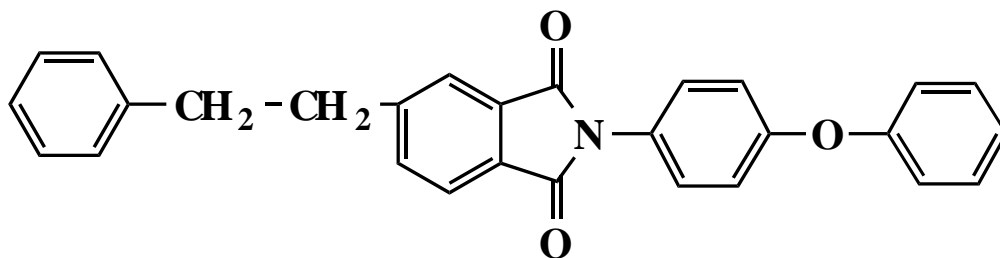
17

phenylethynyl terminated polyimides.^{5,11,14,25,61,110,112,114,118}

Characterization of the cured products of this model compound consist of TLC, HPLC, various methods of NMR analysis, GPC, and MALDI-TOF mass spectroscopy. Results show that in the curing of this compound at 375°C for one hour, reaction products consisted of compounds which were not only of higher molecular weight but also fragments of the starting compound were obtained. Complex and detailed NMR studies of both proton and carbon spectra lead to the identification of these fragments, **18**, and also of a reduction product, **19**.



18



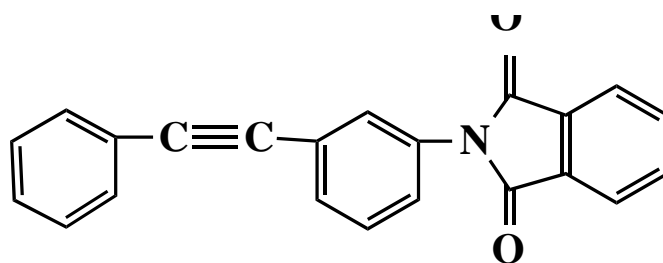
19

Investigations into the curing products of this model compound will be continued. It has been proposed that these aliphatic containing compounds, **18** and **19**, could either be due to insignificant side reactions or they could be critical initiating species in the formation of higher molecular weight structures.

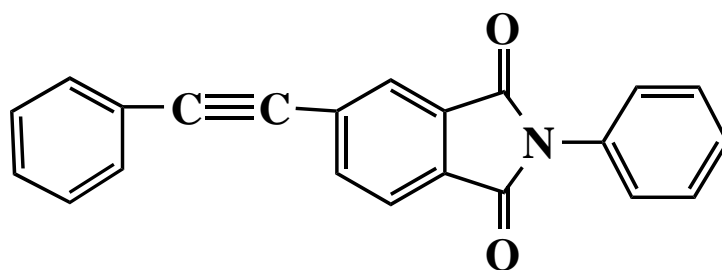
A study was undertaken to investigate the influence of various structural aspects of phenylethynyl compounds on the curing chemistry in 1993.¹²⁴ In this study the relative curing characteristics of a series of di-, tri-, and tetra-phenylethynyl compounds were compared. All of the compounds were made up of a single benzene ring with x number of phenylethynyl substituents. The difunctional species were substituted in the 1,2, 1,3, and 1,4 positions respectively. The trifunctional species were substituted in the 1,2,4 and 1,3,5 positions and the tetrafunctional species was substituted in the 1,2,4,5 positions. These compounds were chosen to compare resonance, steric, inductive and proximity effects on the curing properties. Results obtained by conducting dynamic DSC kinetics experiments showed that the activation energy for the tetrasubstituted compound was the lowest and was equivalent to the activation energies obtained for the 1,2 and 1,4 disubstituted monomers. It was concluded that this was due to resonance stabilization of an initiated radical because it was also found, that of the trisubstituted species, the resonance stabilized 1,2,4 had a lower activation energy than the 1,3,5 which is not stabilized by resonance.

Comparisons of the activation energies of the disubstituted materials also fit with the theory of a resonance stabilized radical. It was unclear why the activation energy for the 1,3,5 monomer was higher than that of the 1,3 but the researchers believed it could be explained by an inductive effect, as there was no resonance possible and steric factors for substitutions in the meta positions were unlikely. These researchers were able to conclude that a resonance stabilized radical is formed more easily in this family of compounds and that this will in turn lower the activation energy of the polymerization. This information could have significance in designing phenylethynyl structures which could be cured at slightly lower temperatures and/or for shorter times.

The curing of two model phenylethynyl compounds has been reported as a comparative effort to evaluate the difference in the curing properties of two popular polyimide endcappers.¹²³ 3-Phenylethynylaniline and 4-phenylethynylphthalic anhydride were reacted with phthalic anhydride and aniline respectively to synthesize the two analogous model compounds, **20** and **21**. The model compounds were cured under vacuum conditions at 320, 340 and 360°C. The cured products were analyzed by HPLC and field-desorption mass spectrometry. The kinetics of the curing of the two model compounds were evaluated by the consumption of the starting material. The kinetics of model compound **20** were determined to fit a second-order plot well while the kinetics



20



21

of model compound 21 better fit to a first-order plot. The validity of these conclusions is not terribly convincing as there were only 3-4 data points for each temperature. One observation that is particularly interesting is that the half lives (table 2.2) of the compounds at the same temperatures do show a large difference indicating that the curing kinetics are very different for the two phenylethynyl compounds. Mass spectrometry indicated that many of the products formed during the curing reaction at 360°C were degradation rather than polymerization products. These degradation products were reported to have molecular mass peaks indicating that the degradative scission was at the acetylenic bonds.

Table 2.2 Half-lives of the Curing Reaction of Phenylethynyl Model Compounds Measured by HPLC¹²³

Compound	half-life at 340°C (min.)	half-life at 360°C (min.)
<u>20</u>	80	30
<u>21</u>	20	6

The authors proposed a theory that the degradation probably took place after an addition polymerization reaction occurred and the fragments were actually degradation products of the dimers, trimers and tetramers formed from reaction of the model compound. Based on the mass spectrometry data the authors proposed the formation of benzyl or phenyl cations due to loss of the pendant phenylethynyl with one or both ethynyl carbons. The stability of these fragments would affect degradation and therefore it should be expected that the 4-phenylethynylphthalic anhydride endcapping agent would show greater thermal stability as the proposed degradation product would be destabilized by the electron withdrawing carbonyl groups in the meta and para positions.

2.5.2 Investigations of Difunctional Phenylethynyl Terminated Polymers

The thermal properties of cured polyimides endcapped with the two endcapping agents used in the previously mentioned study of model compounds **20** and **21** were measured and reported in conjunction with the model compound study.¹²³ A series of 3,000 g/mole polyimides was prepared with an unreactive endcap, phthalic anhydride, used as a control material. The uncured T_g was not reported. After curing of the films at very high temperatures, 370°C or 400°C for 30 minutes or 420°C for 60 minutes the T_g s were measured and reported as

the midpoint of the transition by thermal mechanical analysis. Oddly enough the unreactive endcapper appeared to exhibit an increase in T_g with curing temperature even though this should not be attributed to an increase in crosslink density as with the reactive endcappers. The polymers prepared with the phthalic anhydride and phenylethynylaniline endcapper showed almost identical T_g s after curing at each temperature. The polymer with the phenylethynylphthalic anhydride endcapper showed T_g s about 10°C higher than the other two for each curing temperature. The thermo-oxidative stability was also reported for the cured films by measurement of weight loss over time under isothermal aging in air at 371°C. The stability was reported to follow this order: phthalic anhydride > phenylethynylphthalic anhydride > phenylethynylaniline, with weight retentions after aging at 500 hours being largely different and on the order of 95, 65 and 35% respectively. This research indicates that there is a difference in the cure kinetics and degradation mechanisms of the phenylethynyl groups when the immediate electronic environment is changed and gives some insight into what types of structures may be more desirable for obtaining optimum cured properties.

A more recent publication reported a DSC study of a 4-phenylethynylphthalic anhydride terminated polyimide.¹¹⁸ DSC measurements were conducted in both air and nitrogen for this polyimide and the cure exotherm

was observed to shift to higher temperatures and have a smaller heat of reaction in air. This indicates that the atmosphere during cure could have an effect on the thermoset properties as well as the conditions necessary to achieve full cure. In this case it would appear that the presence of oxygen inhibited the reaction somewhat, possibly by acting as a radical inhibitor. The authors were interested in the correlation between T_g and the residual exotherm for partially cured materials. Some interesting observations were made in this study. First, at very low reaction times at 372°C, 2 and 4 minutes, the T_g increased over the uncured material but the heat of reaction was actually larger than the initial exotherm. The authors proposed that this was an indication that probably more than one reaction was taking place and that the observed exotherm was a compilation of these reaction heats. A second observation that the T_g of the material continued to increase after no residual exotherm was observed. Linear extrapolation of the correlated T_g and residual exotherm heat provided a T_g which was 10°C lower than the measured T_g of the fully cured material. This indicates that reactions to create crosslinks may be occurring after all of the endgroups have reacted.

A study comparing some curing and thermal stability properties of polyimides endcapped with 4-phenylethynylphthalic anhydride derivatives was reported in 1994.¹¹² A series of phenylethynyl endcappers was prepared which had substituents in the para position to the ethynyl group on the pendant phenyl

ring of 4-phenylethynylphthalic anhydride. The substituents were all electron withdrawing except for the hydrogen on the control unsubstituted endcapper. The substituents were: CF_3 , COC_6H_5 , CN and F . A series of polyimide oligomers made using these endcappers was synthesized and studied. DSC measurements showed that the electron withdrawing substituted polyimides each displayed an onset of cure and a cure maximum temperature lower than the control. Samples of the 7,000 g/mole polymers were cured at 370, 400 or 420°C for one hour. This curing cycle produced materials which all had a T_g of 360°C at 420°C cure temperature. The lower curing temperature provided consistent differences in the T_g . At 370°C cure the T_g s were in the following order with substituents: CF_3 , $\text{H} < \text{COC}_6\text{H}_5 < \text{CN}, \text{F}$. At the 400°C cure temperature the order of the T_g s was similar, $\text{H} < \text{CF}_3, \text{COC}_6\text{H}_5 < \text{CN}, \text{F}$ and the F and CN had reached the maximum T_g observed of 360°C. These results indicate that there is a difference in the curing of these polymers either mechanistically and/or kinetically. These high temperatures may also produce possible degradative mechanisms. These researchers measured the thermo-oxidative stability of the cured films in air at 371°C and found that the weight retention after 1500 hours ranged from about 77% for the COC_6H_5 and F substituted systems to about 85% for the unsubstituted and CN substituted systems. The weight retention of the CF_3 substituted system was intermediate between these two values. Thus, there was not a clear

correlation between the cure temperature and the weight retention of the materials after aging.

Chapter 3-Experimental

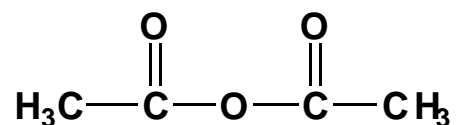
3.1 -Introduction

This chapter includes the experimental methods used in the synthesis and characterization of the phenylethynyl monomers, phenylethynyl terminated oligomers and the resulting thermosets. Purification of reagents and solvents is of critical importance in the controlled synthesis of polymers and is discussed first. The synthesis or acquisition of monomers as well as their respective purification methods is included second. The syntheses of controlled molecular weight polymers using both the weak base and strong base systems are illustrated with representative experiments. The characterization techniques used to study the monomers and the polymeric material properties are included last in this chapter.

3.2- Purification of Reagents and Solvents

3.2.1 -Solvent Acquisition and Purification

3.2.1.1- Acetic Anhydride



F.W.=102.0898 g/mole

bp = 138-140°C

-purchased from Aldrich Chemical and Fisher Chemical

-used from the bottle as received

3.2.1.2- Triethylamine



F. W.= 101.19 g/mole

bp=89°C, d=0.726

-purchased from Fisher in 99% purity

-distilled from calcium hydride at 1 atm and stored under nitrogen atmosphere

3.2.1.3- Methanol



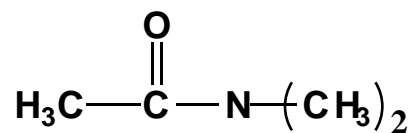
F.W.=32.04 g/mole

bp=64.7°C

-purchased from Fisher Chemical in reagent grade

-used as received for deprotection of phenols and polymer precipitations

3.2.1.4- N,N-Dimethylacetamide



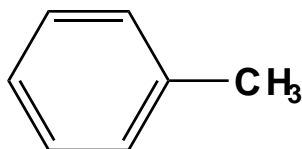
F.W.=87.12 g/mole

bp=164.5-166°C

-purchased from Fisher Chemical in reagent grade

-stirred over calcium hydride for 12 hours then distilled under vacuum and stored under a nitrogen atmosphere in a sealed flask until use

3.2.1.5- Toluene



F.W.=92.14 g/mole

bp=110°C

-purchased from Fisher Chemical in reagent grade

-used from the bottle as received

3.2.1.6- Chloroform



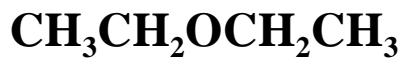
F.W.=119.38 g/mole

bp=61°C

-purchased from Fisher Chemical in reagent grade

-used from the bottle as received

3.2.1.7- Diethyl Ether



F.W.=74.12 g/mole

bp=34.6°C

-purchased from Fisher Chemical in reagent grade

-used as received primarily for work-up

3.2.1.8- Hexanes



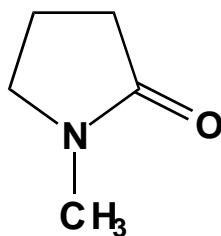
F.W.=86.18 g/mole

bp=68-70°C

-purchased from Fisher Chemical in reagent grade

-used as received primarily for monomer work-up and recrystallizations

3.2.1.9- 1-Methyl-2-Pyrrolidone



F.W.=99.13 g/mole

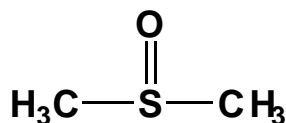
bp=81-82°C/10mm

-purchased from Fisher Chemical in reagent grade

-stirred over P₂O₅ overnight, distilled under vacuum and stored in a sealed flask

under a nitrogen atmosphere until used

3.2.1.10- Dimethyl Sulfoxide



F.W.=78.13 g/mole

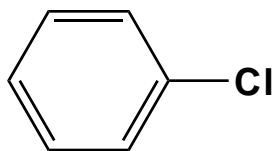
bp=189°C

-purchased from Fisher Chemical in reagent grade

-stirred over calcium hydride overnight, distilled under vacuum and stored in a

sealed flask under a nitrogen atmosphere until used

3.2.1.11- Chlorobenzene



F.W.=112.56 g/mole

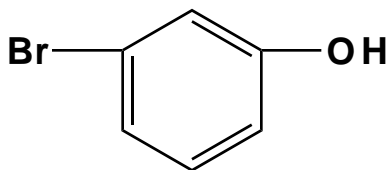
bp=132°C

-purchased from Fisher Chemical in reagent grade

-used without further purification

3.2.2 Reagent Acquisition and Purification

3.2.2.1- 3-Bromophenol



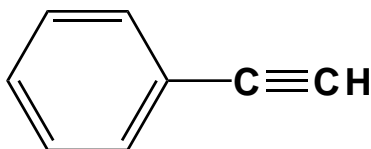
F.W.=173.01 g/mole

mp =30-32°C

-purchased from Aldrich Chemical in 98% purity

-used from the bottle as received

3.2.2.2- Phenylacetylene



F. W.=102.14 g/mole

bp=142-144°C, d=0.930

-purchased from Aldrich Chemical in 98% purity

-distilled under aspirator vacuum $\approx 45^{\circ}\text{C}$ into a dry ice/IPA cooled receiving flask and stored wrapped in foil under a nitrogen atmosphere in a refrigerator

3.2.2.3- Bis(triphenylphosphine)Palladium(II) chloride



F.W.=701.89 g/mole

-purchased from Aldrich Chemical in 99.99% purity

-stored in brown bottle in a dry desiccator until used as received

3.2.2.4- Copper(I) Iodide

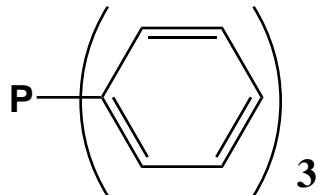


F. W.=190.44 g/mole

-purchased from Aldrich Chemical in 99.999% purity

-stored in brown bottle in a dry desiccator until used as received

3.2.2.5- Triphenylphosphine



F.W.=262.29 g/mole

-purchased from Aldrich Chemical in 99% purity

-stored in a dry desiccator until used as received

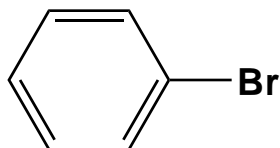
3.2.2.6- Potassium Carbonate



F.W.=138.21

- purchased from Aldrich Chemical in 99+% purity
- stored in a dessicator and used as received for deprotection of phenols
- used after drying at 120°C overnight under vacuum for polymerization of Poly(arylene ether sulfone)s

3.2.2.7- 4-Bromobenzene



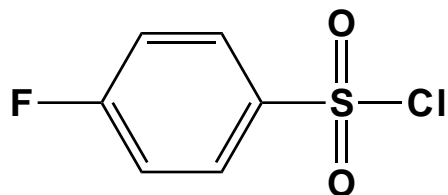
F.W.=157.02 g/mole

bp=156°C

d=1.491

- purchased from Aldrich Chemical in 99+% purity
- distilled from calcium hydride using aspirator vacuum at 56°C and stored in a sealed flask under nitrogen

3.2.2.8- 4-Fluorobenzenesulfonylchloride



F.W.=194.61

mp=35-38°C

bp=95-96°C/2mm

-purchased from Aldrich Chemical in 98% purity

-distilled under pump vacuum at 77-78°C into ice cooled flask and stored in a sealed flask under nitrogen atmosphere

3.2.2.9- Aluminum Chloride

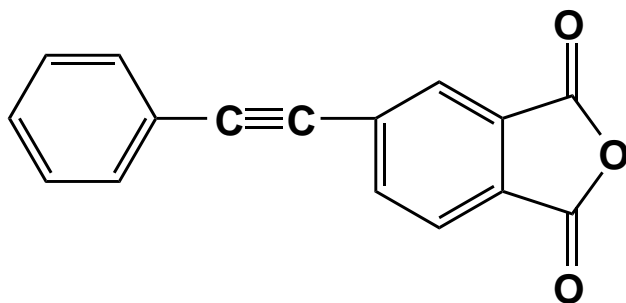


F.W.=133.34 g/mole

-purchased from Fisher Chemical in 99% purity

-used from the bottle as received

3.2.2.10- 4-Phenylethynylphthalic Anhydride

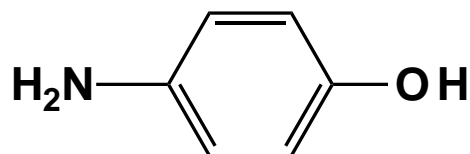


-F.W.=248.2374 g/mole

mp=150-151°C

-Synthesized by Dr. Biao Tan using a published procedure^{11,134} -used as
received

3.2.2.11- 4-Aminophenol



F.W.=109.13 g/mole

mp=188-190°C

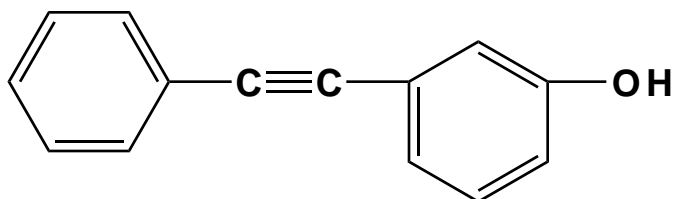
-purchased from Aldrich Chemical in 98+% purity

-used as received from the bottle

3.3 Synthesis, Acquisition and Purification of Monomers

3.3.1 Monofunctional Endcappers

3.3.1.1- 3-Phenylethynylphenol



FW.=194.2324

mp=86-87°C

Synthesis of this monofunctional endcapper was carried out in the following three step procedure.

Synthesis of 3-Phenylethynylphenol

1) Protection of 3-Bromophenol-

To a 500 mL 3 neck round bottom flask with a condenser, magnetic stir bar and nitrogen flow was added 70.5 g 3-bromophenol (0.407 moles) and 115 mL acetic anhydride (1.22 moles). The reaction vessel was stirred and placed in a oil bath at 150°C. The reaction refluxed at 145°C for 2 hours after which it

was removed from the bath and cooled. The light yellow solution was transferred to a 1L Erlenmeyer flask and 2 x 250 mL portions of distilled water were added slowly with stirring. When the temperature returned to ambient the solution was extracted with 4 X 400 mL of diethyl ether. The combined ether layers were washed with 4 x 500 mL and 3 x 1L of distilled water to remove any remaining acetic acid or acetic anhydride. The ether was then removed by rotary evaporation to provide pure 3-bromophenylacetate.

2) Oxidative Addition of Phenylacetylene and 3-Bromophenylacetate-

A 1L 3 neck round bottom flask was fitted with a condenser, overhead stirrer and nitrogen inlet and flamed dry under nitrogen atmosphere. 84.93 g of 3-bromophenylacetate (0.395 moles), 51.99 g of phenylacetylene (0.509 moles) and 0.963 g of triphenylphosphine (0.0037 moles) were added into the reaction vessel with 530 mL of triethylamine. The stirring was begun and the reaction vessel was surrounded by a tent of aluminum foil and the lights were turned off in the room. 0.471 g of bis(triphenylphosphine)palladium(II)chloride (0.0007 moles) and 0.190 g of copper(I) iodide (0.001 moles) were added into the reaction vessel with 30 mL of triethylamine in the dark. The reaction was heated to 120°C and stirred for ≈12 hours in the dark. The reaction was removed from the heat and the white precipitate was filtered and washed with triethylamine.

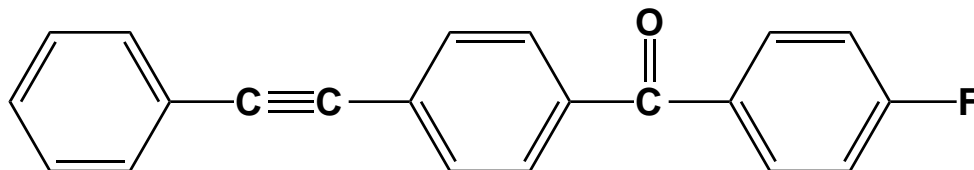
The yellow filtrate was placed in a rotary evaporator and the triethylamine was removed, to provide a brown oil which slowly crystallized affording the crude 3-phenylethynylphenylacetate.

3) Deprotection of Crude 3-Phenylethynylphenylacetate-

To a 1L round bottom flask equipped with a overhead stirrer, condenser and nitrogen inlet was added 120 g of 3-phenylethynylphenylacetate (0.5 mole), 120 g of potassium carbonate (0.87 moles) and 600 mL of methanol. The reaction was allowed to reflux in a 90°C oil bath for 4 hours. The reaction was cooled and added to water. The methanol was largely removed by rotary evaporation leaving a mixture of dark oil and water. 0.2 % aqueous hydrochloric acid was added to the mixture slowly until the pH was reduced to ≈ 9 . The oil solidified and was easily removed from the water as a solid. The water was extracted with ether and the ether was removed by rotary evaporation to provide a dark oil which slowly crystallized. Both the crude forms of 3-phenylethynylphenol were purified by recrystallization with large amounts of hexanes. The material was heated in hexanes to the saturation point. The insoluble oil was either filtered or decanted from the hot orange solution. Activated charcoal was added to the hexanes and the solution was filtered through celite and allowed to crystallize overnight at room temperature. White crystals

of pure 3-phenylethynylphenol were filtered and dried in the vacuum oven at room temperature.

3.3.1.2- 4-Fluoro-4'-Phenylethynyl-4-Benzophenone



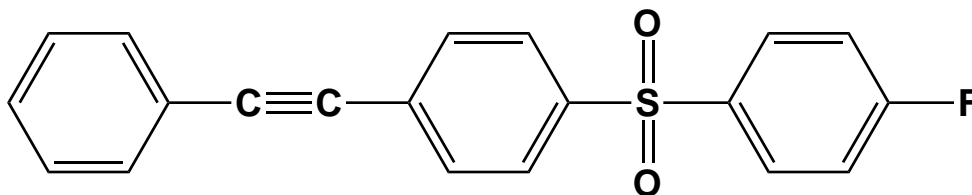
-F.W.=300.3315 g/mole

mp=151°C

-received as a pure sample courtesy of Dr. John W. Connell⁶³ (NASA Langley)

-used after drying at 80°C under vacuum overnight

3.3.1.3- 4-Fluoro-4'-Phenylethynyldiphenylsulfone



F.W.=336.3799 g/mole

mp= 189°C

This compound was synthesized in a two step procedure where the first step involved a Friedel Crafts sulfonylation and the second a metal catalyzed oxidative addition of the brominated carbon on the Friedel Crafts product to phenylacetylene.

Synthesis of 4-Fluoro-4'-Phenylethynyldiphenylsulfone

1) Synthesis of 4-Bromo-4'-Fluorodiphenylsulfone-

To a 100 mL 3-neck round bottom flask equipped with a overhead stirrer, nitrogen inlet and a water condenser with needle sized nitrogen outlet was added 15.3711 g of solid 4-fluorobenzenesulfonylchloride (0.07893 moles) and 30 mL of bromobenzene (0.28487 moles) as the solvent. 10.7344 g, a 2 mole % excess, of aluminum chloride (0.08050 moles) was added slowly with no visible exotherm. The reaction flask was purged with nitrogen and placed in a heated oil

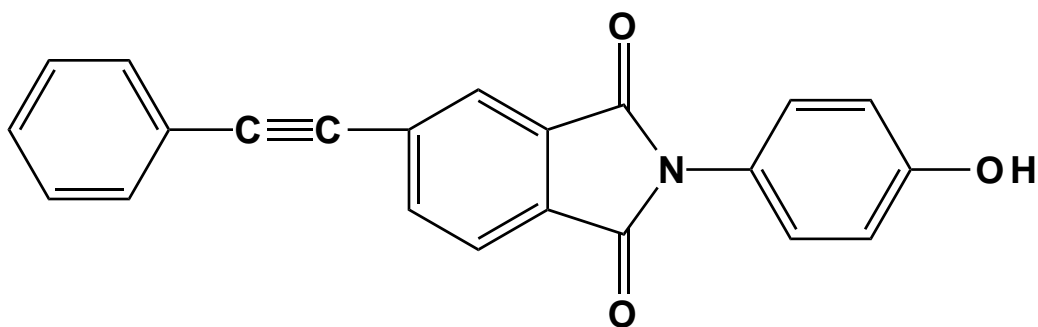
bath at 160°C. The reaction temperature stabilized at 140°C. Hydrochloric acid vapor was removed through the needle outlet and the reaction was allowed to react for three days. A very small amount of hydrochloric acid was still detected at the nitrogen outlet. The reaction was cooled and poured into 300 mL of hydrochloric acid/ice water and stirred. When the ice had melted, 300 mL of chloroform was added and the immiscible mixture was added to a 2,000 mL separatory funnel. The water layer was extracted with 2 more portions each of 100 mL of chloroform. The three chloroform layers were combined and washed with water. The chloroform was then rotovapped to give an orange liquid which slowly crystallized to a solid. The orange solid was recrystallized in hexanes containing charcoal to provide 10.6167 g (0.03369 moles) of 4-bromo-4'-diphenylsulfone. The dried white crystals were obtained in a yield of 43%.

2) Oxidative Addition of 4-Bromo-4'-Fluorodiphenylsulfone and Phenylacetylene-

To a flamed and purged 250 mL 3 neck round bottom flask equipped with an overhead stirrer, condenser with nitrogen outlet and nitrogen inlet was added 11.8594 g of 4-bromo-4'-fluorodiphenylsulfone (0.03763 moles), 0.0918 g of triphenylphosphine (0.0003499 moles) and 30 mL of triethylamine. The mixture was heated with stirring in a 60°C oil bath. Next, 5.37 mL of phenylacetylene

(0.04890 moles) was added into the reaction vessel along with 15 mL of dry NMP, which promoted formation of a solution. Next, 0.0449 g of bis(triphenylphosphine)palladium(II)chloride (0.00006 moles) and 0.0179 g of copper(I) iodide (0.00009 moles) were added to the reaction in the dark with 20 mL of triethylamine. The reaction was stirred, purged and heated for 12 hours in the dark, then cooled and filtered. The solid was washed with diethyl ether into the filtrate and placed in a rotary evaporator to remove the bulk of the solvent. The semi-solid material remaining was dried at 80°C in the vacuum oven to provide some crude 4-fluoro-4'-phenylethyndiphenylsulfone. The reaction precipitate was dissolved in 100 mL chloroform and washed with 4 x 100 mL of distilled water in a separatory funnel to remove the salt. Evaporation of the chloroform provided the bulk of the product. The crude material from both portions was dissolved in chloroform and added dropwise to an excess of hexanes to promote crystallization. Cooling in ice water induced more of the product to crystallize. The pure white crystals were filtered and dried at 80°C in the vacuum oven.

3.3.1.4- 4-Phenylethynylphthalimidophenol



-F.W.= 339.3496, mp=283°C

-pure compound was dried at 120°C under vac. overnight before use

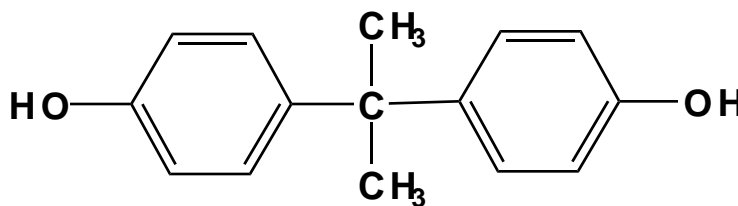
The synthesis of this compound was carried out in one step by imidization of phenylethynylphthalic anhydride with 4-aminophenol.

Synthesis of 4-Phenylethynylphthalimidophenol (PEPIP)

To a 100 mL 3 neck round bottom flask equipped with a overhead stirrer, nitrogen inlet and a toluene filled dean stark trap with a condenser was added 10.1008 g of 3-phenylethynylphthalic anhydride (0.040284 moles) and 4.8895 g of 4-aminophenol (0.0443124 moles) with 30 mL of DMAc and 25 mL of toluene. The reaction vessel was kept under a nitrogen purge, stirred and placed in an oil bath at 170°C. Toluene (15 mL) was removed to bring the refluxing temperature of the reaction to 145°C. After 6 hours the reaction was cooled at which time it essentially solidified into a yellow gold solid. This was filtered and

washed with 1L of diethyl ether to provide a light yellow solid which was dried in the vacuum oven at 120°C overnight. The crude PEPIP was dissolved in a ≈95/5 vol/vol mixture of chloroform and trifluoroacetic acid. This solution was immersed in an ice water bath and cyclohexane was added dropwise to induce crystallization of the pure product. When the maximum amount of white crystals were present they were filtered and dried.

3.3.1.5- Bisphenol A

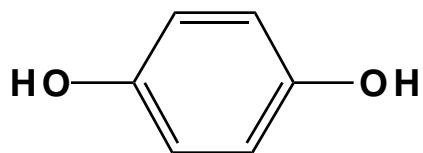


F.W.=228.29 g/mole

mp=159°C

- received as a sample from Dow Chemical in monomer grade purity
- dried under vacuum at 80°C overnight before use in polymerizations

3.3.1.6- Hydroquinone



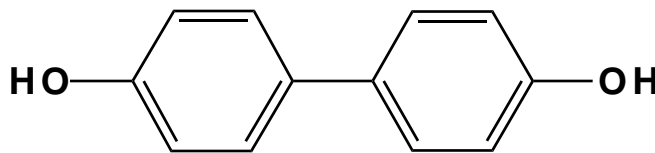
F.W.=110.11 g/mole

mp=175°C

-received as a sample from Eastman Chemical in monomer grade purity

-dried under vacuum at 60°C overnight before use in polymerizations

3.3.1.7- 4,4'-Biphenol



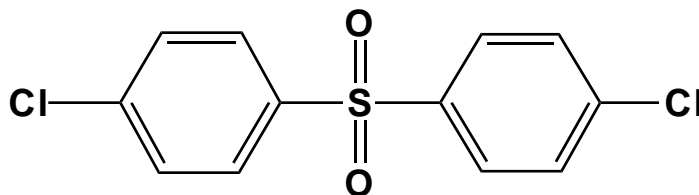
F.W.=186.21

mp=284°C

-received as a sample from Amoco Chemical in monomer grade purity

-dried under vacuum at 60°C overnight before use in polymerizations

3.3.1.8- 4,4'-Dichlorodiphenylsulfone



F.W.=287.17 g/mole

mp=149°C

-received as a sample from Amoco Chemical in monomer grade purity

-dried under vacuum at 80°C overnight before use in polymerizations

3.4 Phenylethynyl Terminated Poly(arylene ether sulfone)s

3.4.1 Molecular Weight and End-group Control in Polymers

Molecular weight and endgroups were controlled by offsetting the stoichiometry of two difunctional monomers, the bisphenol and the activated dihalide and adding enough monofunctional monomer to react with the monomer in excess. The well established equations developed by Carothers¹³⁵ were used to determine the relative amounts of monomers to incorporate into the polymers synthesized in this research. These equations are provided below.

$$X_n = 1/(1-p) \quad X_n = \text{degree of polymerization}$$

(As $p \rightarrow 1$, X_n gets very large)

p = extent of fraction of conversion of the functional groups

$$X_n = 1+r/(1-r)$$

$$r = N_A/N_B \quad N_X = \text{number of X functional groups}$$

when using a monofunctional endcapper:

$$r = N_A/(N_B + N_B') \quad N_B' = \text{number of monofunctional groups}$$

3.4.2 Synthesis of a Phenylethynyl Terminated Poly(arylene ether sulfone) Via Potassium Carbonate

A series of oligomers which varied in molecular weight and composition was prepared via the synthesis shown in Figure 3.1. Both homopolymers using the three different bisphenols and wholly aromatic copolymers using various ratios of 4,4'-biphenol and hydroquinone were synthesized through the following procedure.

The synthesis of a 3-phenylethynylphenol (PEP) terminated, 50:50 mole % Hydroquinone (HQ): 4,4'-Biphenol (BP) containing, 5,000 g/mole poly(arylene ethersulfone) oligomer will be illustrated as a representative example of the synthetic experiments. The reaction vessel utilized was a 4 neck 250 mL round bottom flask equipped with an overhead stirrer, toluene filled dean-stark trap, with condenser, temperature probe and nitrogen inlet. The condenser was covered with a septa and a needle was inserted to allow an outlet for the nitrogen purge. The flow of nitrogen was regulated with a needle valve and a bubbler to about 1-2 bubbles per second. To the reaction vessel was added 3.000 g of HQ (0.02725 moles), 5.0733 g of BP(0.02725 moles), 16.9370 g of 4,4'-dichlorodiphenylsulfone (DCDPS) (0.05898 moles), 1.7446 g of PEP (0.00898 moles) and 9.2127 g K_2CO_3 (0.06665 moles) (about 5% molar excess) were added quantitatively and washed in with 106 mL NMP followed by 50 mL toluene. The

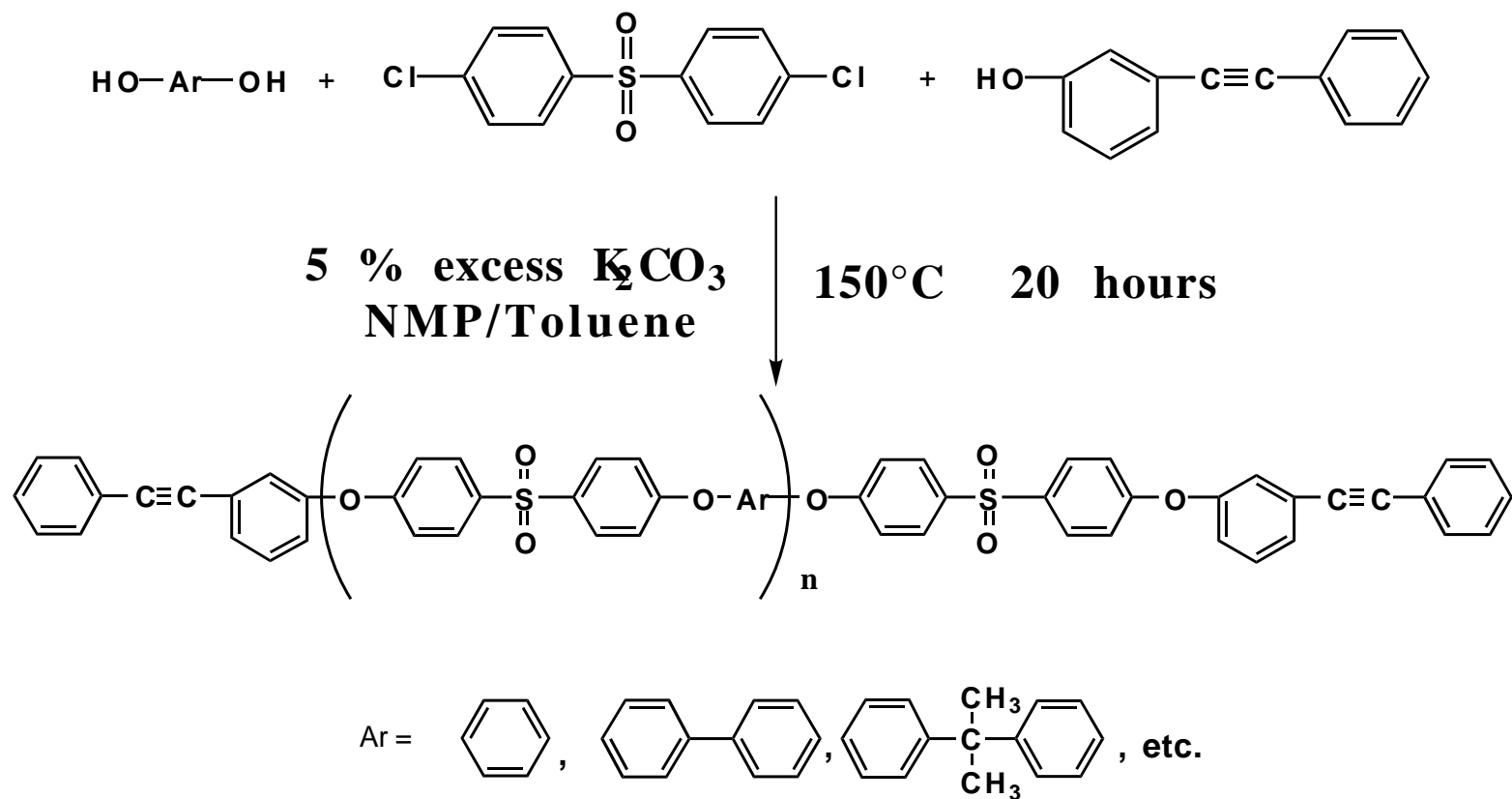


Figure 3.1-Synthesis of Phenylethynylphenol Terminated Poly(arylene ether sulfone) Oligomers with Potassium Carbonate

reaction vessel was placed in a silicone oil bath at 175°C and the stirrer was applied at a rate sufficient to disperse the insoluble base and resulting salt without splashing the reaction contents into the joints. The amount of reflux occurring in the DS trap was observed to be very small when the dark colored solution temperature was stable at 143°C. To increase the solution temperature and therefore the reflux rate, a small amount (about 5 mL at a time) of toluene was removed from the DS trap. After removal of about 10 mL of toluene the solution temperature increased to about 149-150°C and the reflux rate was rapid. After about one hour of refluxing the color of the solution was a green/brown color which continued to darken over the reaction time presumably due to some degradation of the NMP. Over the next few hours some water was accumulated in the DS trap. Slowly, as toluene was removed from the system the solution temperature increased. For example, after 4 hours the temperature had increased to 151°C and the reflux was somewhat slower. After 24 hours the solution temperature was 156°C and the reflux was negligible. The reaction was removed from the oil bath and filtered through a buchner funnel with coarse filter paper to remove the insoluble salt. To the black/brown solution was added 0.70 mL of acetic acid (0.0121 moles) to neutralize the excess base used in the synthesis. The solution was then precipitated into a mixture of about 80:20 methanol:water, filtered and dried at about 150°C in a vacuum oven. The dried polymer was

redissolved at 20% solids in chloroform to produce a cloudy solution. This solution was filtered through a 1.2 micron filter in a pressure filter apparatus to remove the salt precipitate. The resulting clear yellow solution was precipitated into pure methanol and dried at a temperature just below T_g overnight to remove the last traces of solvent.

Some small amount of the salt appeared to be soluble in the NMP reaction solvent. For all of the fully amorphous polymers reprecipitation from chloroform after filtering was a good method for removal of this salt. The semi-crystalline polymers were found to be insoluble in chloroform or chlorobenzene and therefore this method was not available in those cases. The insoluble polymers were stirred in room temperature water for one hour to remove the salt. Both of these methods were deemed to be successful as judged by elemental analysis for potassium

3.4.3 Synthesis of a Phenylethynyl Terminated Poly(arylene ether sulfone) Via Sodium Hydroxide

The strong base synthetic method has a few distinct differences from the weak base synthetic method. First of all the sodium hydroxide can form the diphenate of the bisphenol monomer at room temperature and it is strong enough to easily promote hydrolysis of the activated dihalide. Therefore the strength of

the base requires consideration of the solubility of the diphenate in the reaction solvent as well as its precise stoichiometry. Thus, the activated dihalide can't be added into the reaction until all of the strong base has been reacted to form diphenate ions and the aqueous by product is removed. It was found that the bisphenates of 4,4'-biphenol and hydroquinone were insoluble in NMP, making this synthetic method unusable for these reactants. However, the bisphenate of bisphenol A was found to be soluble so this was a viable method for this reactant as pointed out some years ago by Johnson et. al.⁹ The synthesis of this polymer is illustrated in Figure 3.2. A representative experiment will be detailed for the synthesis of a 3,000 g/mole phenylethynyl terminated bisphenol A poly(arylene ether sulfone) using sodium hydroxide as a strong base.

To a 100 mL 3 neck round bottom flask equipped with a reverse dean stark trap with a condenser and nitrogen outlet, an overhead stirrer and an addition funnel with nitrogen inlet was added 5.1588 g bisphenol A(0.022597 moles) and 1.6206 g of 3-PEP (0.0083438 moles) with 20 mL of DMSO and 40 mL of chlorobenzene. The reactants and solvents were stirred under nitrogen while 2.144 g of sodium hydroxide (0.053539 moles) was added slowly and quantitatively in the form of a previously titrated aqueous solution. The reaction vessel was placed in a oil bath at 170°C and stirred to begin the dehydration.

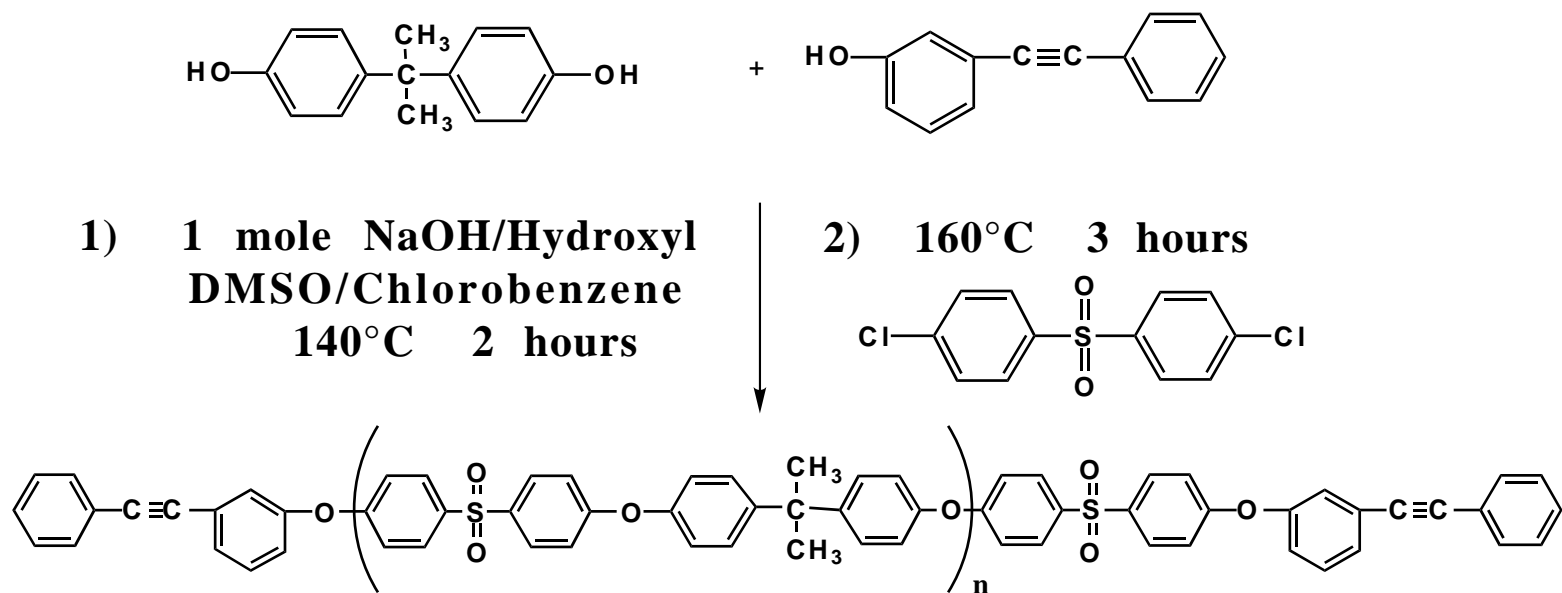


Figure 3.2 Synthesis of Phenylethynyl Terminated Poly(arylene ether sulfone) Using Sodium Hydroxide as the Base

After one hour the reaction was refluxing at 128°C and it had an opaque green/yellow appearance. 10 mL of chlorobenzene was removed from the reverse dean stark trap and the bath temperature was increased to 175°C. The reflux temperature increased quickly to 138°C. After 10 min. at this temperature the reaction vessel was removed from the oil bath to stop the reflux long enough to change the reverse dean stark trap with a column containing 1 gram of calcium hydride drying agent wrapped in filter paper. During this cooling step some solid precipitate formed on the walls of the reaction vessel. The reaction was brought to reflux again at 138°C and held there with the drying column for one hour. The reverse dean stark trap was replaced and chlorobenzene was removed until the reaction temperature was 155-160°C. At this point the reaction was opaque and light bright yellow. After refluxing at 160°C for one more hour there was no evidence of more water evolving. The reaction was an opaque mustard yellow with white solid precipitate. 7.6871 g of DCDPS (0.026769 moles) was dissolved at 20% solids in 30 mL of chlorobenzene and added slowly to the reaction through the addition funnel, maintaining the reflux temperature above 150°C. Immediately after the initial addition of DCDPS solution the reaction turned clear and produced a brown/green precipitate on the walls of the vessel. During the addition of the DCDPS solution over 30 minutes, most of the precipitate was washed into the reaction. The final reflux temperature was 163°C

and the clear solution was a amber/brown color. The reaction was allowed to reflux at this temperature for an additional 1.5 hours. The reaction was then cooled, filtered to remove the sodium chloride and diluted with 15 mL of DMSO. The clear solution was precipitated into a 80:20 mixture of methanol:water, producing a powdery precipitate which was filtered and dried before reprecipitation from chloroform.

As was previously mentioned the stoichiometry of the sodium hydroxide solution is very important for obtaining the molecular weight control in the reaction. This is more easily accomplished in a large scale reaction similar to what is carried out on an industrial scale. On a small scale even a small discrepancy can disrupt the stoichiometry enough to prevent molecular weight and endgroup control. A 50 wgt % aqueous solution of sodium hydroxide was prepared and stored in a sealed flask under nitrogen. The solution was titrated with a 0.13054 N hydrochloric acid solution to provide an accurate normality for the sodium hydroxide solution. The normality of the hydrochloric acid solution was determined by titrating a dry sodium carbonate standard. The sodium hydroxide solution was then added to the reaction quantitatively using a micrometer syringe with a 2 mL capacity and 0.5% accuracy.

3.5- Manufacture of Composite Panel

A 6" X 6" X 0.113" carbon fiber fabric composite panel was prepared in the laboratories of Prof. A.C. Loos using a 3,000 g/mole bisphenol A based phenylethynyl terminated poly(arylene ether sulfone) powder as the matrix material. A AS4-PW-3k carbon fiber fabric with G-sizing (believed to be an epoxy) was used as the fiber material. In a 6" X 6" mold was placed first 6 plies of fabric then 14.3 g of powder was spread evenly across it. Another two layers of each was then added on top of the first layers. All 18 plies of the carbon fabric had the warp directions parallel to each other. The top was placed on the mold and the mold was placed in the programmable hot press. The panel was consolidated at 370°C for 2 hours at 150 psi. The heating and cooling rates in the press were 3°C/min.

3.6- Characterization

This section details the techniques used to characterize the monomers, the phenylethynyl terminated poly(arylene ether sulfone) oligomers and the corresponding thermosets produced in this thesis.

3.6.1 Nuclear Magnetic Resonance Spectroscopy (NMR)

NMR spectroscopy was measured on a Varian Unity 400 MHz instrument. Solvent choice was determined by solubility of the compounds. Most of the samples were prepared from deuterated chloroform, deuterated dimethyl sulfoxide or hydrogenous NMP. Deuterated chloroform was used as the first choice when possible. The only deviation from these solvent systems was in the characterization of phenylethynylphthalimidophenol. In this one case it was necessary to add about 5% trifluoroacetic acid to 95% chloroform to obtain a solution.

3.6.1.1 ^1H NMR

This technique was predominantly used to verify structure and purity of monomers. In addition $\langle \text{Mn} \rangle$ could be calculated from the ratio of endgroup to repeat unit protons. In most cases the aromatic region of the spectra was very crowded and it was necessary to use quantitative ^{13}C NMR for this calculation.

Samples were made in a concentration of 100 mg/0.7 mL of solvent and placed in a 5 mm NMR tube after solvation.

3.6.1.2 Quantitative ^{13}C NMR

The experiments to obtain quantitative integrations for the ^{13}C spectra were conducted in cooperation with Mr. Tom Glass in the NMR analytical services department. The samples were prepared in a concentration of 300 mg/3.0 mL of solvent and were added to a 10 mm NMR tube after solvation. $\langle M_n \rangle$ could be calculated from the ratio of endgroup to repeat unit carbons. To minimize error due to inconsistent integrations and baselines, the M_n was calculated as an average of the M_n values obtained from the ratios of all the well defined peaks in each spectrum.

3.6.2 Gel Permeation Chromatography

GPC measurements for the poly(arylene ether sulfone) oligomers were conducted in either chloroform or NMP in cooperation with Dr. Q. Ji.

GPC in NMP was measured on a Waters 150C equipped with an infrared detector as well as a viscosity detector. The combination of these detectors allows for universal calibration and the measurement of absolute molecular weights.

The samples were run in NMP with 0.02 mole % P_2O_5 at 60°C.^{136,137}

Chloroform analyses were run at 30°C on a Waters GPC instrument equipped with a Viscotek DV100 viscosity detector and a Viscotek Laser DRI refractive index detector. The columns for both solvents were Waters Styragel HT3 + HT4 and the flow rate was 1 mL/min.

3.6.3 Potentiometric Titrations

Potentiometric titration was used to monitor phenylethynyl terminated poly(arylene ether sulfone) oligomers for the presence of phenolic endgroups.¹³⁸⁻¹⁴⁰ A MCI GT-05 Automatic Titrator was used to carry out the titrations. The oligomers were dissolved in NMP and titrated with a 0.05 N solution of tetramethylammonium hydroxide (TMAH). The TMAH titrant was standardized with potassium hydrogen phthalate immediately before the titrations. When using NMP as the sample solvent it was necessary to titrate a blank of the same NMP to the potential found for the sample titrations. The volume necessary to reach this potential was subtracted from each sample titration to determine the amount of titrant necessary for the phenolic endgroups.

3.6.4 Differential Scanning Calorimetry

DSC was used to determine the glass transition temperatures (T_g) of the phenylethynyl terminated poly(arylene ether sulfone) oligomers and the cured

thermoset films. A Perkin Elmer Model DSC7 was used for the measurements. The scans were run in nitrogen at 10°C/min. and the T_g values were taken as the midpoint of the endotherm from the second heat in all instances. In the cases where the oligomers were semi-crystalline the T_m was taken from the first heat.

It was necessary to take the first heat above the T_m but not to the curing temperature which would raise the T_g on the second heat. In the case of the amorphous oligomers it was only necessary to heat to 20-30°C above the T_g in the first heat.

3.6.5 Thermogravimetric Analysis

Dynamic TGA was performed on a Perkin Elmer TGA7. The experiments were performed in air with a heating rate of 10°C/min. Weight loss of the sample was measured as a function of time and temperature. The dynamic TGA experiments were used to monitor dryness of the oligomers samples and 5 % weight loss values were calculated from completely dry samples.

3.6.6 Melt Rheology

Rheological measurements were carried out on a Bohlin VOR rheometer with a 12 mm diameter parallel plate fixture.^{62,141,142} Temperature control was accomplished with a Bohlin HTC using nitrogen as the heating gas. Samples

of the uncured powder were prepared by pressing a pellet about 1 mm thick in a mold at room temperature. The measurements were collected in the oscillation mode at 0.1 Hz under both dynamic and isothermal temperature conditions. The dynamic temperature ramp was 3°C/min in all cases.

3.6.7 Single Lap Shear Measurements

Lap shear samples were prepared by producing an E-glass cloth impregnated plaque of 85 wt. % polymer which was then cured in a hot press at 370°C for 1-2 hours between two Pasa-Jel or chromic acid anodized treated titanium 6Al-4V plates. A chloroform solution of the amorphous oligomers was used to prepare the lap shear samples while the semi-crystalline oligomers were prepared from an NMP solution. The titanium 6Al-4V plates were primed with NMP/polymer solution immediately after the surface treatment was completed and the samples were prepared and tested within a couple of days of the priming procedure in all cases. An Instron-1123 was used to test the samples following the ASTM-D1002 method with a crosshead speed of 0.05 in/min.

3.6.8 Infrared Spectroscopy

FTIR was used to monitor the cure reaction of the phenylethynyl moiety. Measurements were taken during the isothermal curing of oligomers at different

temperatures. FTIR spectra were obtained on a Nicolet Impact 400 FTIR spectrometer. Samples were prepared by coating a NaCl disc with a solution of oligomer and evaporating the solvent to leave an oligomer film. A Kapton o-ring was cut and placed around the sample and a clean NaCl disc was placed on top. The sandwich was placed into the heated sample holder at room temperature. The temperature was raised to close to the oligomer T_g and the holder was tightened to ensure that the sample was touching both plates and forming a continuous film. The sample was then placed into the FTIR and heated to the measurement temperature when data was collected. The Omnic Series software was used to collect data with a resolution of 2 inverse centimeters. Each spectrum consisted of 96 scans and was produced every 55 seconds or 64 scans and was produced every 33 seconds. After the experiments were completed the NaCl/thermoset sandwiches were heated in air to 550°C for 2-4 hours to degrade the polymer and leave relatively clean NaCl plates.

3.6.9 Flexural Testing of Composite Panels

Flexural testing of the composite panels was carried out by Mr. Todd Bullions, a Ph.D candidate in Prof. A. Loos research group. Five specimens with dimensions of 4.64" x 1" x 0.113" were cut from the panel with the 4.64" length of the specimen running parallel to the warp direction of the fabric in the panel.

The axes of the loading noses ran perpendicular to the length of the specimens. Each specimen had a support span of 3.62” to give a 32:1 span:depth ratio. A half inch over-hang on each of the specimen was allowed. The testing was carried out as per ASTM D 790-92 for the four point bend test. The loading nose diameters were 0.5” and the cross head speed was 5.43 mm/min. The load span was equal to one third of the support span. The specimen deflection was stopped when load began to decrease and failure had obviously occurred.

3.6.10 Short Beam Shear Testing of Composite Panels

Shear testing of the composite panels was done by Mr. Todd Bullions. Short beam shear tests were conducted on eleven specimens with dimensions of 0.670” X 0.25” x 0.1127”. The 0.670” dimension was running parallel to the warp direction of the fabric in the panel. The axis of the loading nose ran perpendicular to the length of the specimens. Each specimen had a support span of 0.5” to give a 4.4:1 span:depth ratio. A small over-hang on each end of the specimen was allowed. The loading nose diameter was 0.25” and the cross head speed was 1.30 mm/min. The specimen deflection was stopped when load began to decrease and failure had obviously occurred. The peak in the load was obvious by watching the tracking of load by the instron. A few specimens were deflected approximately twice as much as required to achieve peak load to verify that this

was the peak load. The specimens that were removed immediately following the peak load showed little if no signs of damage. Those specimens deflected further displayed horizontal delamination within the specimen at depths ranging from near the center to a few layers below the surface.

3.6.11 Dynamic Mechanical Thermal Analysis

DMTA was conducted in shear mode on thin films of cured phenylethynyl terminated poly(arylene ether sulfone)s by Mr. Mark Muggli, a graduate student in Prof. T.C. Ward's research group. The tests were conducted on a Polymer Laboratories Mark II in a dynamic temperature shear mode from 130°C to 300°C with a heating rate of 3°C/min.

3.6.12 Soxhlet Extraction

Cured films were extracted with chloroform to measure the gel fraction present in each sample. For the measurement of the gel fraction of each film two samples were used and the average value was reported. In all cases the standard deviation was $\leq 2\%$ and was usually closer to 0. The samples were cut into rectangles weighing about 0.2-0.3 g each. The initial weight was accurately measured to four decimal places and recorded. The samples were then placed in a cellulose extraction thimble, which were placed in a soxhlet extraction apparatus where chloroform was refluxed over them for four days. This was

sufficient time to obtain equilibrium weights of the extracted samples. The samples were removed from the thimbles after the solvent was evaporated from them in a hood. The samples were then placed in pyrex beakers and dried in a vacuum oven at about 200°C overnight. After cooling the samples were weighed and this extracted weight was subtracted from the initial weight, divided by the original weight and multiplied by 100 to determine the weight percent gel in the sample.

Chapter 4 Results and Discussion

4.1 Introduction to Results and Discussion

This section presents and discusses results obtained in this research on phenylethynyl terminated poly(arylene ether sulfone)s and the corresponding cured thermosetting networks. Most of the oligomers were synthesized using 3-phenylethynylphenol as the monofunctional endcapping agent and they are referred to as phenylethynyl terminated oligomers. In cases where the endcapper is different from 3-phenylethynylphenol it will be specifically identified as such. The discussion will begin with a definition of the structures of the individual endcappers that have been synthesized. The sections that follow discuss the endgroup and molecular weight control and the curing and physical properties of the phenylethynyl terminated precursor oligomers and the thermoset networks.

4.2 Characterization of Phenylethynyl Endcappers

The mechanism of the curing reaction of the phenylethynyl moiety is challenging and still not well understood.¹²⁰ However, the influence of changing the molecular structure around the reactive site via electron donating or withdrawing groups, on the rate of cure, and network characteristics has been probed with a systematic series of new phenylethynyl endcappers.

4.2.1 3-Phenylethynylphenol (3-PEP)

Synthesis of 3-phenylethynylphenol was achieved via a three step procedure shown in figure 4.1. The first step was the quantitative protection of the phenol group on 3-bromophenol with acetic anhydride. The second step involved metal catalyzed oxidative addition of the protected halogen compound to phenylacetylene to form the diarylacetylene compound, which produced about an 80% yield. Purification of the 3-phenylethynylphenylacetate was carried out by sublimation of the orange crystals, or in some cases the crude product was deprotected with base before purification of 3-phenylethynylphenol by recrystallization with hexanes containing charcoal. Structural characterization of the pure final compound is presented here.

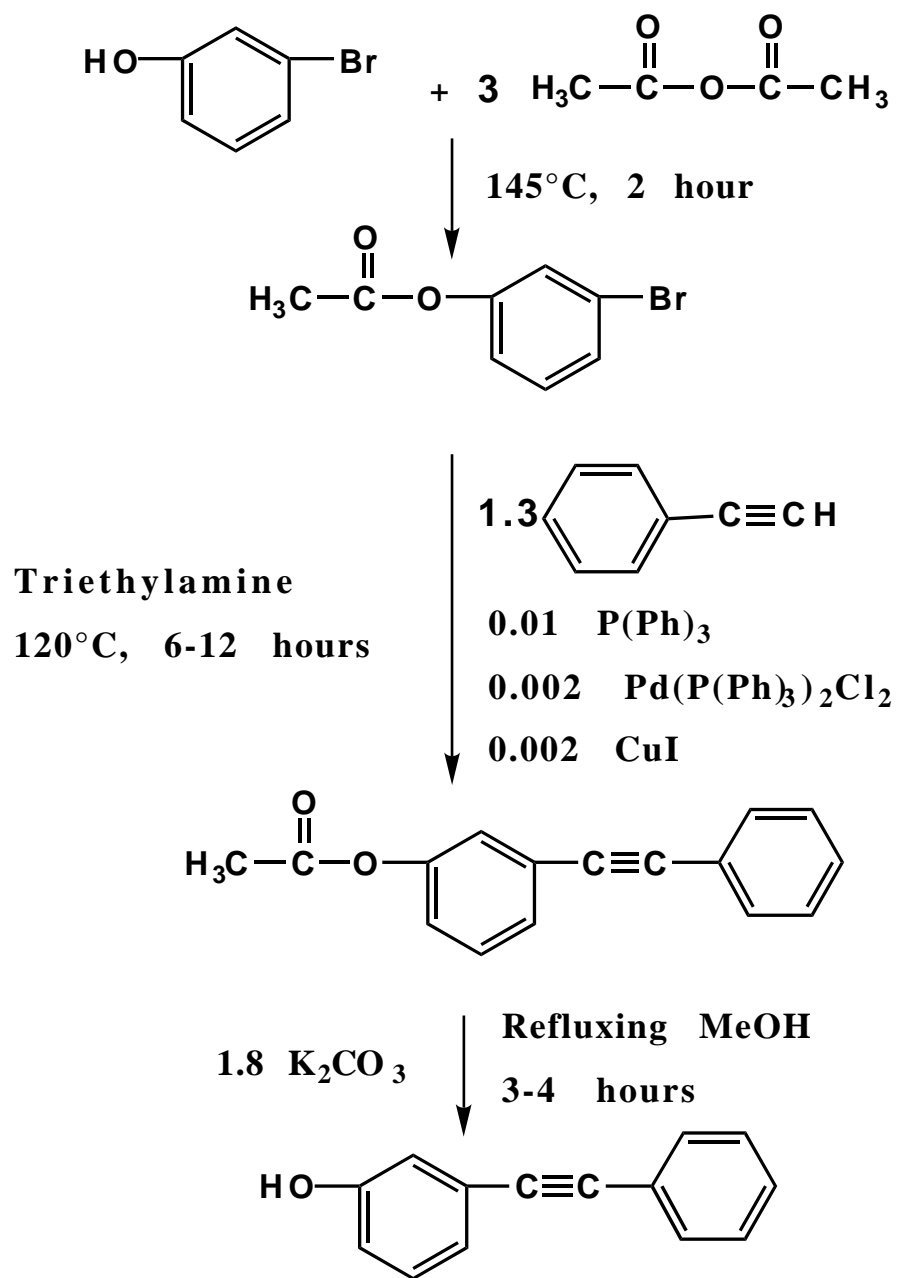


Figure 4.1-Synthesis of 3-Phenylethynylphenol

The aromatic region of the ^1H NMR spectra of 3-PEP is shown in Figure 4.2. The peaks are labeled and the integrations agree with the expected ratios. The FTIR spectrum is shown in Figure 4.3. The ethynyl stretch appears as a weak band at about 1950 cm^{-1} . A medium intensity peak is seen at about 950 wavenumbers that could correspond with aromatic C-H bending in the vicinity of the phenylethynyl ring. This peak is also present and well defined in the phenylethynylphenol oligomers and disappeared after curing.

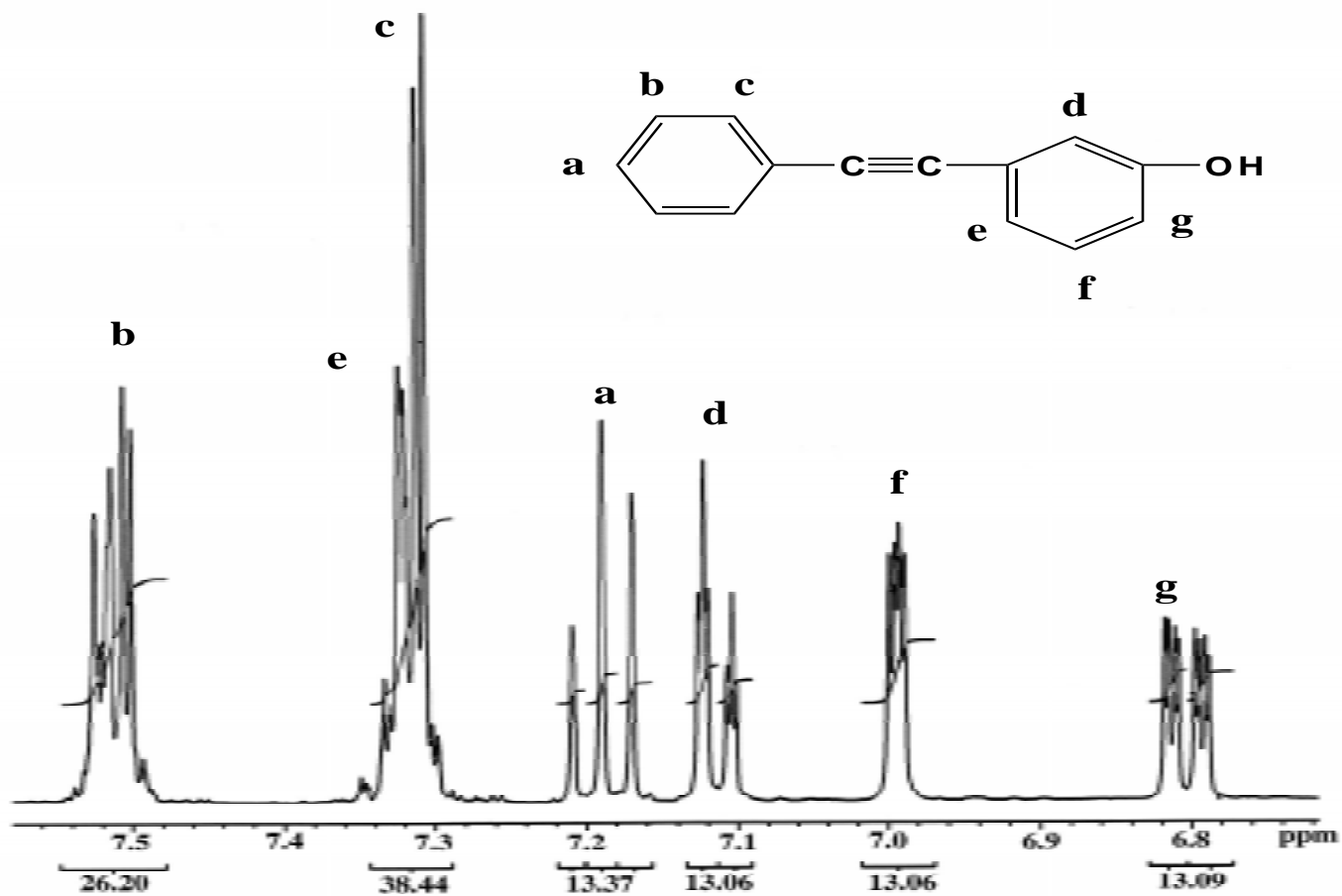


Figure 4.2 - ^1H NMR Spectrum of 3-Phenylethynylphenol in Deuterated Chloroform

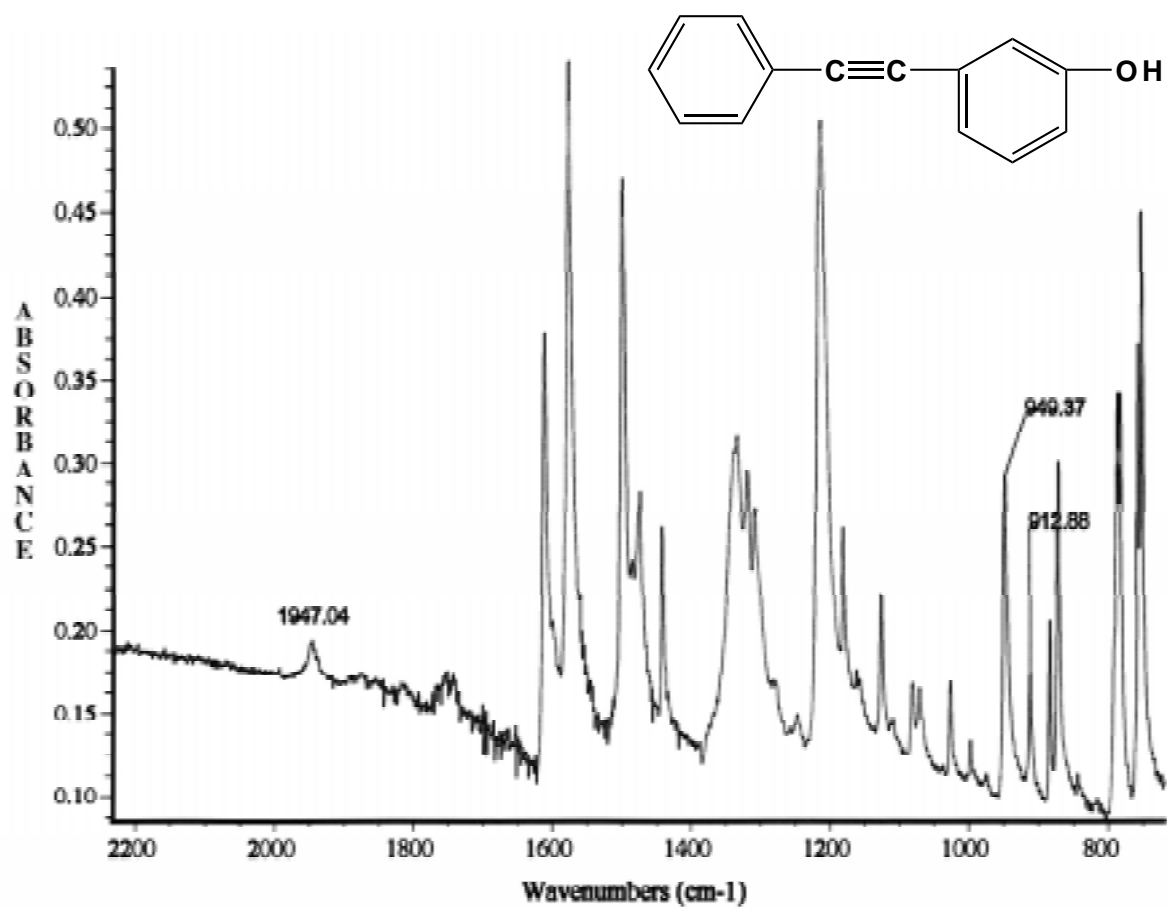


Figure 4.3 -FTIR Spectrum of 3-Phenylethynylphenol (KBr Pellet)

4.2.2 4-Fluoro-4'-phenylethynylbenzophenone (FPEB)

This compound was received as a monomer grade sample from Dr. Connell at NASA Langley. The synthesis of this compound has been described in a previous publication.⁶³ Palladium catalyzed oxidative addition of 4-bromo-4'-fluorobenzophenone to phenylacetylene was accomplished in a similar manner to the oxidative addition reaction in the synthesis of 3-phenylethynylphenylacetate in section 4.2.1. Purification of FPEB was reportedly accomplished by recrystallization from acetone. The structural characterization is presented here.

The aromatic region of the ¹H NMR spectrum of FPEB is shown in Figure 4.4. The peaks are labeled with the corresponding protons and the integrations are correct for the proposed structure. The FTIR spectrum is shown in Figure 4.5. A strong peak is present in the FTIR at about 1650 wavenumbers which corresponds to the ketone carbonyl stretch. The ethynyl stretch is a weak intensity peak at 2217 cm⁻¹. Strong peaks seen at 1150 and 1220 cm⁻¹ are likely due to the aromatic C-F stretch.

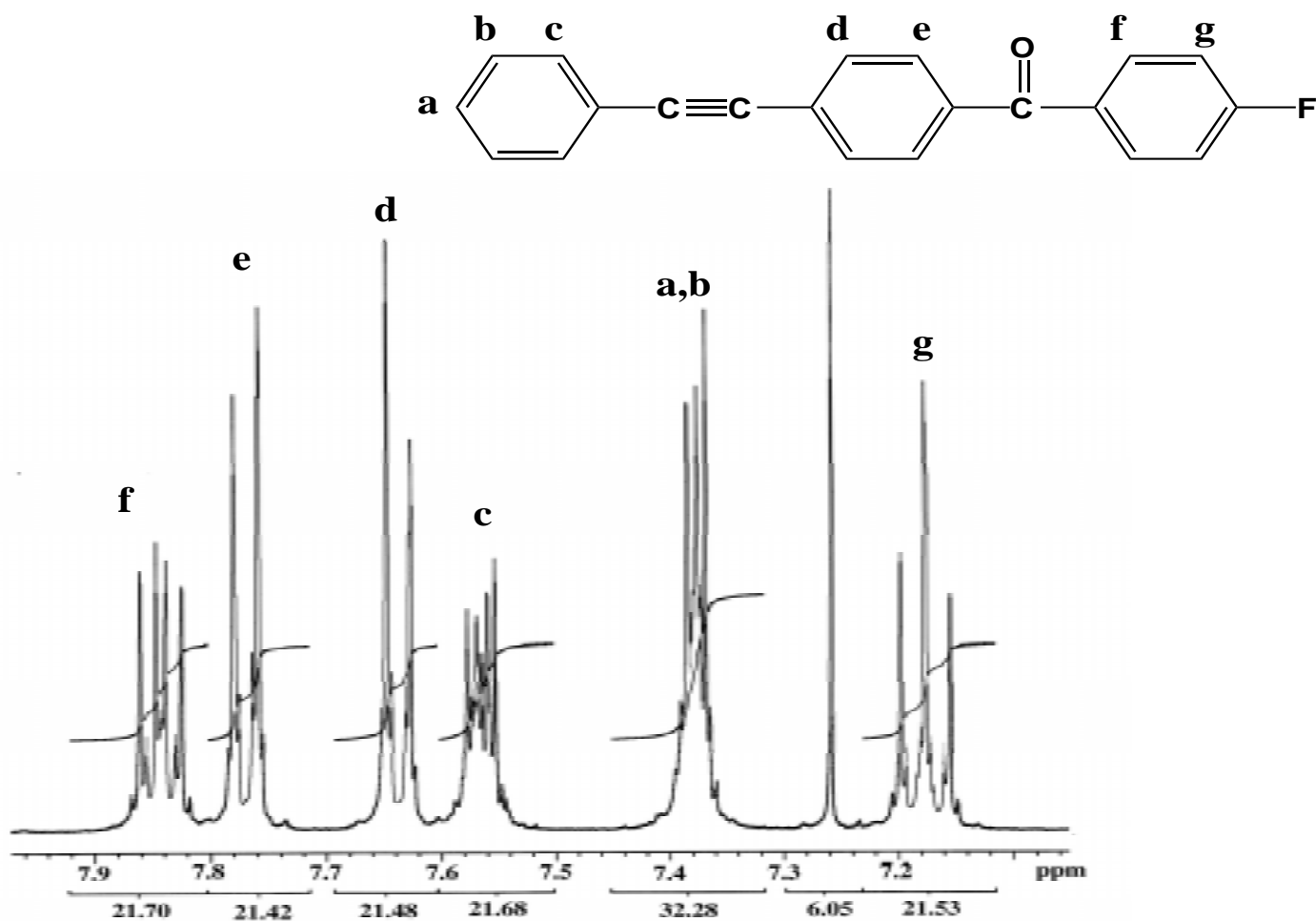


Figure 4.4 ^1H NMR Spectrum of 4-Fluoro-4'-phenylethynyl-benzophenone in Deuterated Chloroform

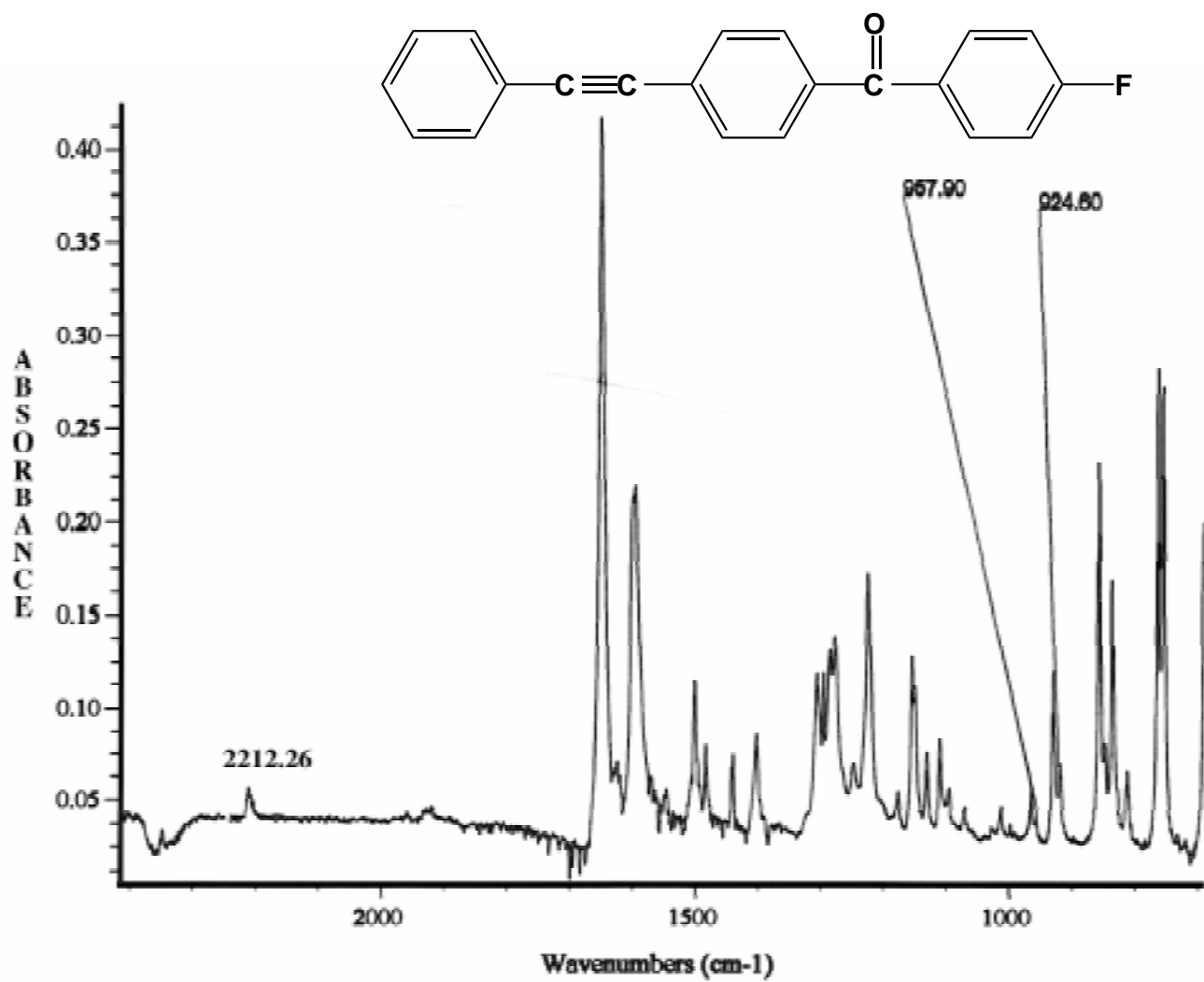


Figure 4.5 -FTIR Spectrum of 4-Fluoro-4'-phenylethynyl-benzophenone (KBr Pellet)

4.2.3 4-Fluoro-4'-phenylethynyldiphenylsulfone (PEFDPS)

The synthesis of PEFDPS was carried out in a single step by the palladium catalyzed oxidative addition of 4-bromo-4'-fluorodiphenylsulfone to phenylacetylene as shown in figure 4.6. The synthesis of 4-bromo-4'-fluorodiphenylsulfone was accomplished using an aluminum chloride catalyzed Friedel-Crafts sulfonylation of 4-fluorobenzene sulfonyl chloride with bromobenzene. This reaction was very slow even at elevated temperatures, near the reflux temperature of bromobenzene and a purified yield of only 43% was achieved after 3 days reaction time. Previous experiments indicated that the reaction was still progressing even after 4 days. Recrystallization of the crude yellow crystals from hexanes with activated charcoal provided white crystals which appeared pure by TLC and ^1H NMR. The white crystals were used for the oxidative addition reaction to produce the phenylethynyl terminated endcapper.

The procedure for the synthesis of the phenylethynyl endcapper was slightly different from the synthesis of 3-phenylethynylphenylacetate from 3-bromophenylacetate. Triethylamine is used as a solvent in the reaction because it will form a salt with the bromine ion produced during the reaction. The starting material for this reaction, 4-bromo-4'-fluorodiphenylsulfone was insoluble in pure triethylamine. Increasing the temperature to the reaction temperature of 60°C increased the solubility, but not enough to make a completely clear solution.

In order to get this monomer into solution with the phenylacetylene it was necessary to add distilled NMP. The solvent ratio was then 23% NMP/77% triethylamine. An excess of triethylamine was still present and the reaction was slightly more dilute than for the previous syntheses of related compounds.

The workup of this compound was also complicated by solubility issues. Typically, the reaction is cooled and a white/yellow precipitate was observed in a yellow solution. This solution was not clear on cooling, but was opaque. Filtration of the solid provided a clear yellow solution in which it was later found there was very little product. Most of the product was filtered out as a solid with the salt. The solid was dissolved in chloroform and washed repeatedly with water to remove the salt. The chloroform was then removed and the bulk of the product was found in this portion. Both portions were purified by induced cold crystallization in hexanes from chloroform solution to provide pure white crystals.

The aromatic region of the ^1H NMR spectra of PEFDPS is shown in Figure 4.7. The peaks are labeled and the integrations are correct. The FTIR spectrum is shown in Figure 4.8. The sulfone stretch appears in two very strong peaks at 1155 and 1320 cm^{-1} . The ethynyl stretch is a low intensity sharp peak at 2220 cm^{-1} . The peak at 1155 is likely overlapping the peak due to the C-F stretch.

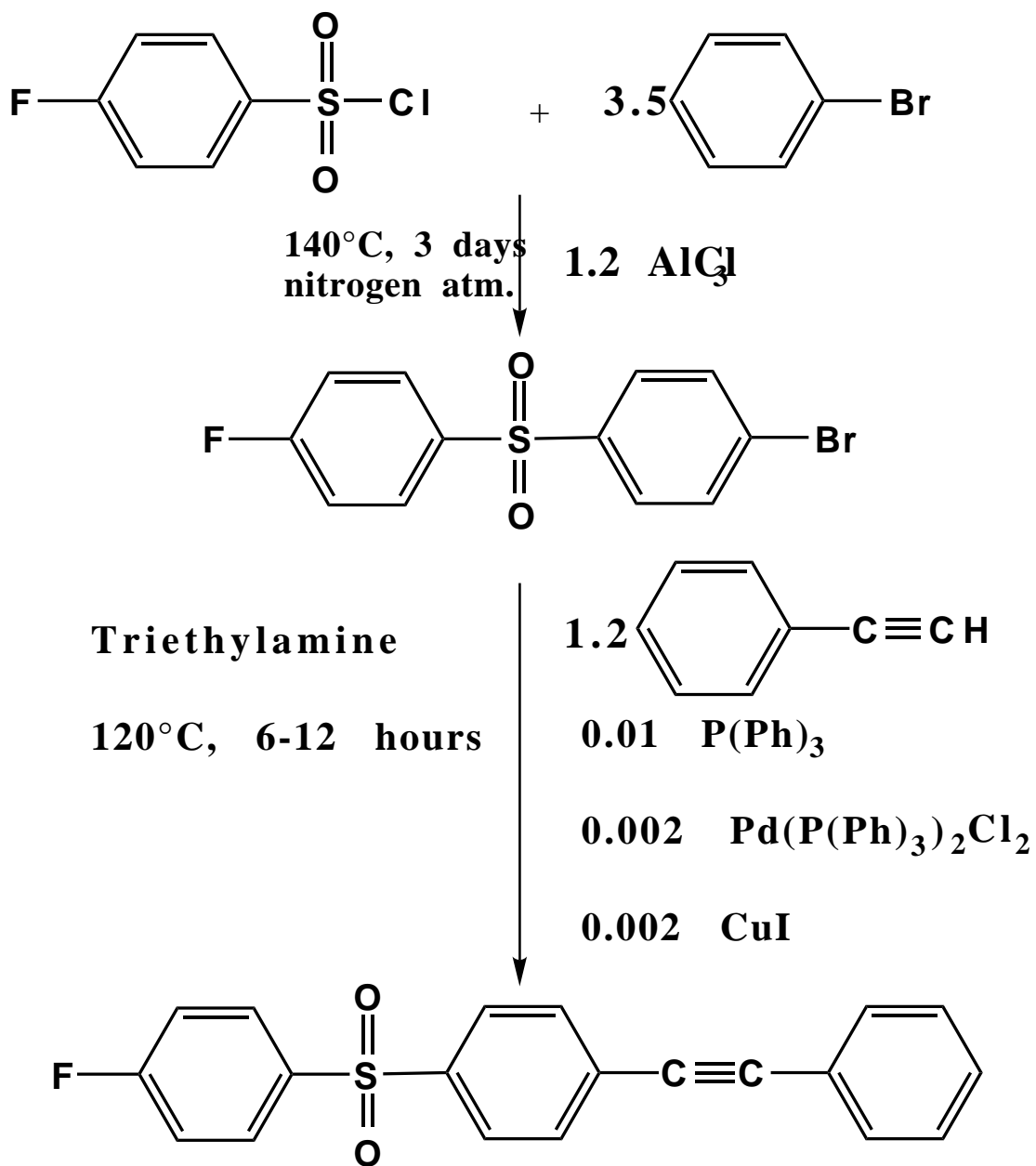


Figure 4.6 - Synthesis of 4-Fluoro-4'-phenylethynyldiphenylsulfone

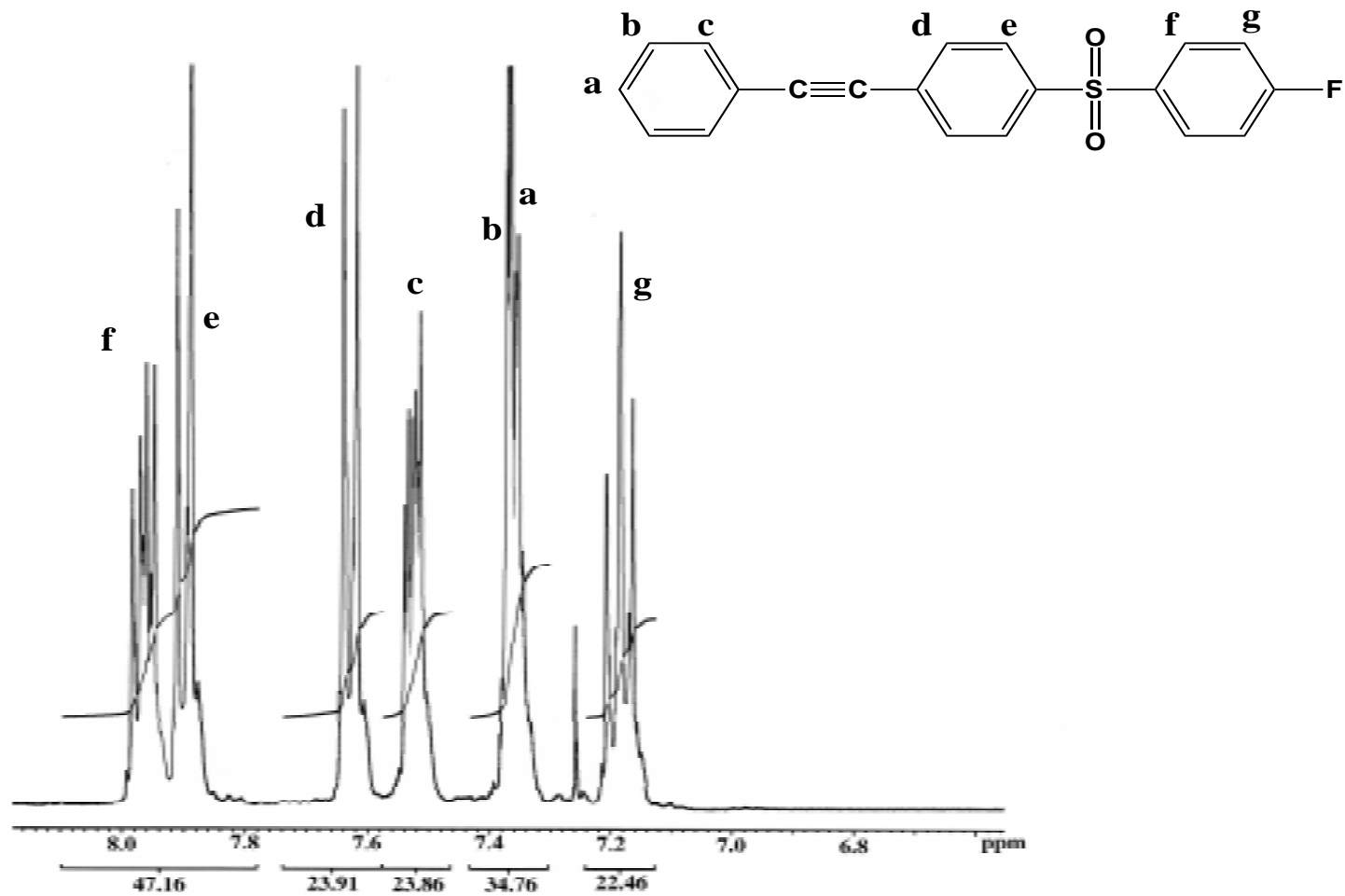


Figure 4.7 ^1H NMR Spectrum of 4-Fluoro-4'-phenylethynyl-diphenylsulfone in Deuterated Chloroform

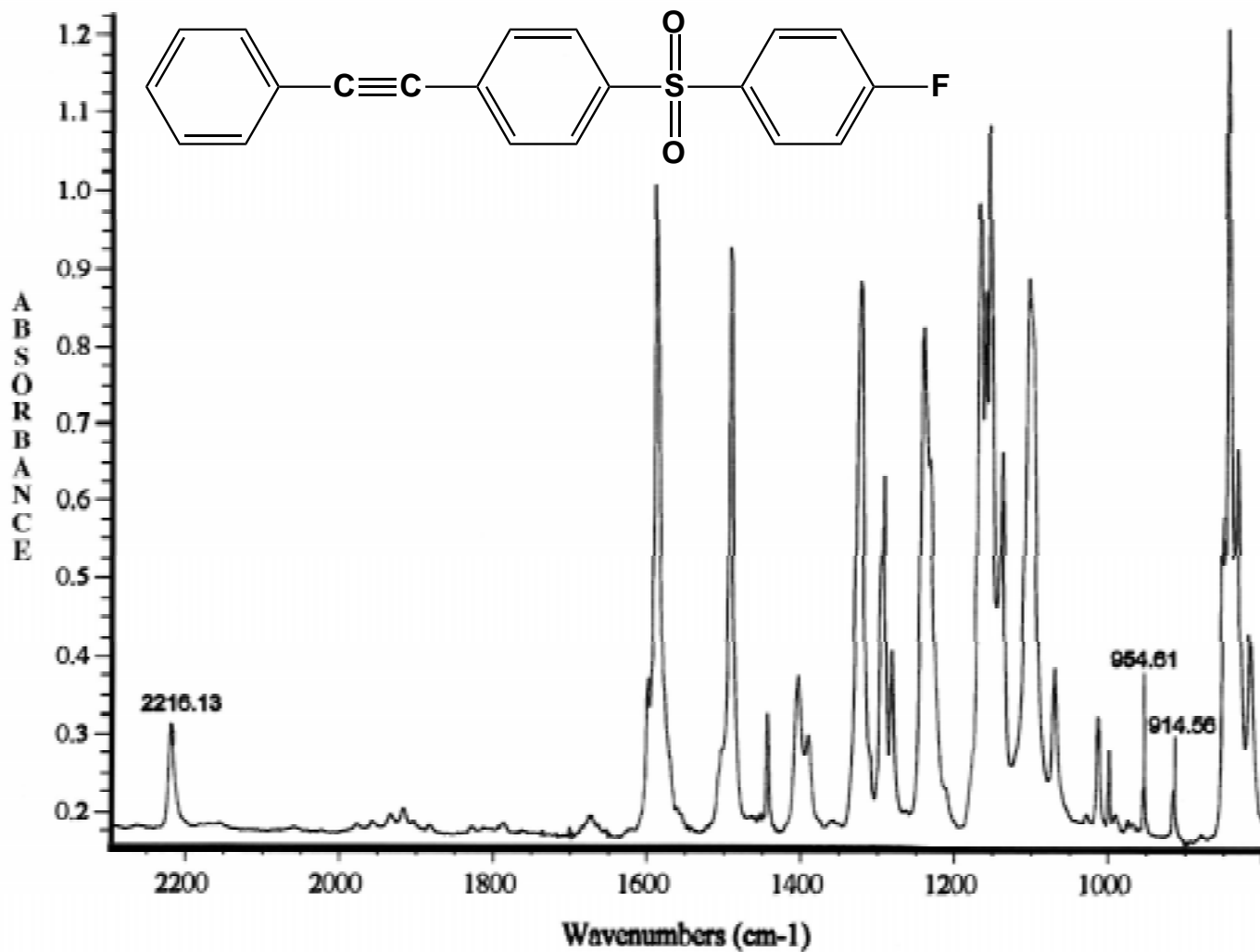


Figure 4.8 -FTIR Spectrum of 4-Fluoro-4'-phenylethynyl-diphenylsulfone (KBr Pellet)

4.2.4 Phenylethynylphthalimidophenol (PEPIP)

Synthesis of PEPIP was carried out by the one step solution imidization of phenylethynylphthalic anhydride with 4-aminophenol to produce a crude yellow compound which was easily purified by inducing crystallization from the chloroform/trifluoroacetic acid solution with a small amount of added cyclohexane. This method of purification afforded small white crystals. The reaction scheme is shown in figure 4.9.

The aromatic region of the ^1H NMR spectra of PEPIP is shown in Figure 4.10. The peaks are labeled with the corresponding protons and the integrations are correct for the structure shown. The FTIR spectrum is shown in Figure 4.11. The imide carbonyl stretch appears at two peaks, 1724 (strong) and 1774 (medium) cm^{-1} . The ethynyl stretch is a low intensity sharp peak at 2212 cm^{-1} .

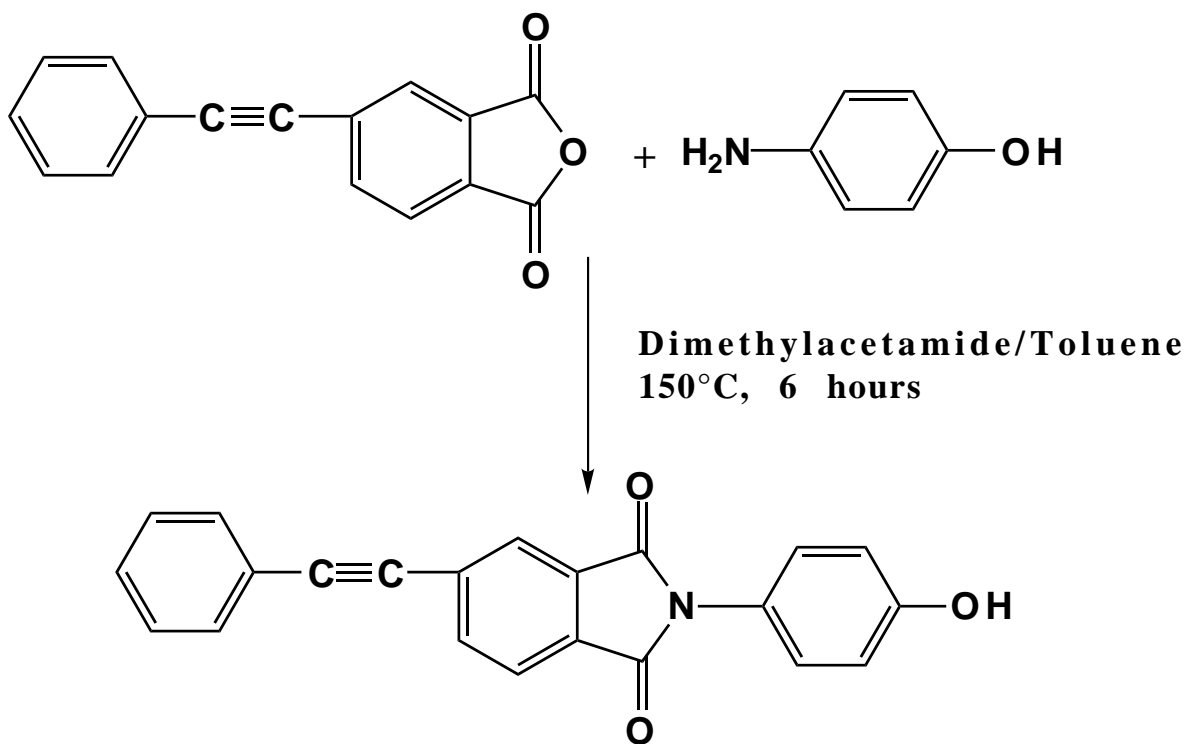


Figure 4.9 -Synthesis of 3-phenylethynylphthalimidophenol

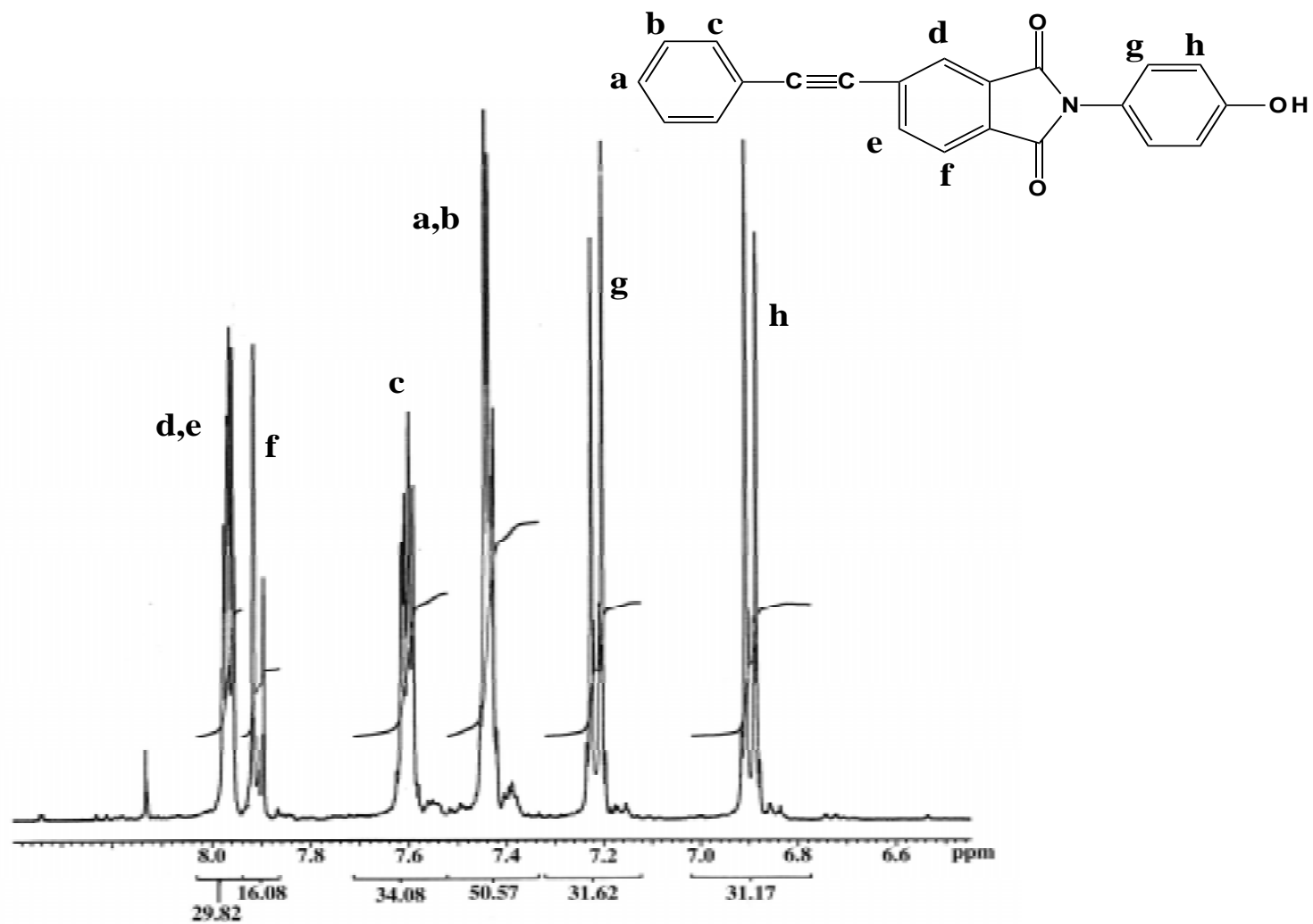


Figure 4.10 ¹H NMR Spectrum of Phenylethynylphthalimidophenol in Deuterated Chloroform

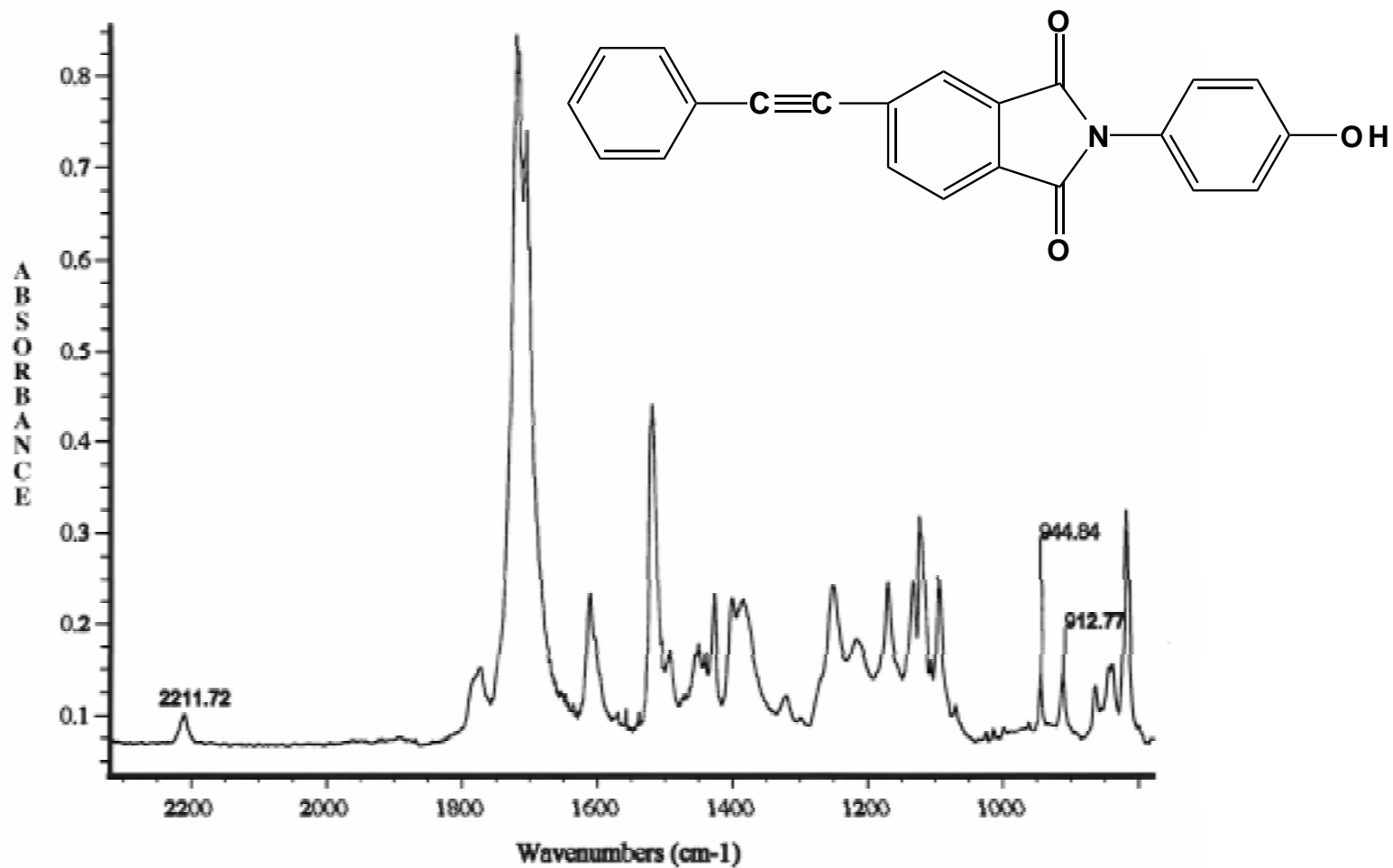


Figure 4.11 -FTIR Spectrum of Phenylethynylphthalimidophenol (KBr Pellet)

4.2.5 Comparison of the Structures of the Monofunctional Endcapper Molecules

All of the endcapper molecules described above contain a diphenylacetylene moiety. All of the molecules have substitution on one of the phenyl rings only, either in the meta or para, or both, positions. The para substituted positions allow for the stronger resonance effects across the ring, whereas the meta substituted positions only allow for the weaker inductive effects. The effect that the electronic character of the substituents has on the ethynyl carbons can be seen by ^{13}C NMR. It has been suggested that it is possible to glean two types of information from the shifts of the acetylenic carbons in substituted acetylenes.¹⁴³ Firstly, the difference in the shifts of the ethynyl carbons can be compared to the unsubstituted alkyne. This gives some indication of the relative electronic charge in the triple bond. The second type of information is from the difference in the shifts of the two ethynyl carbons, $\text{C}\beta\text{-C}\alpha$, where the $\text{C}\alpha$ is on the unsubstituted phenyl ring and $\text{C}\beta$ is on the substituted one in the diphenylacetylene derivative. This value provides information on the relative polarization of the bond by the given substituents. Figure 4.12 provides the ^{13}C NMR spectra of the ethynyl region of the four different diphenylacetylene derivatives used in this research. The ^{13}C shifts for the ethynyl carbons are listed in Table 4.1. The difference in the shifts can be a measure of the polarizability of the ethynyl bond by the

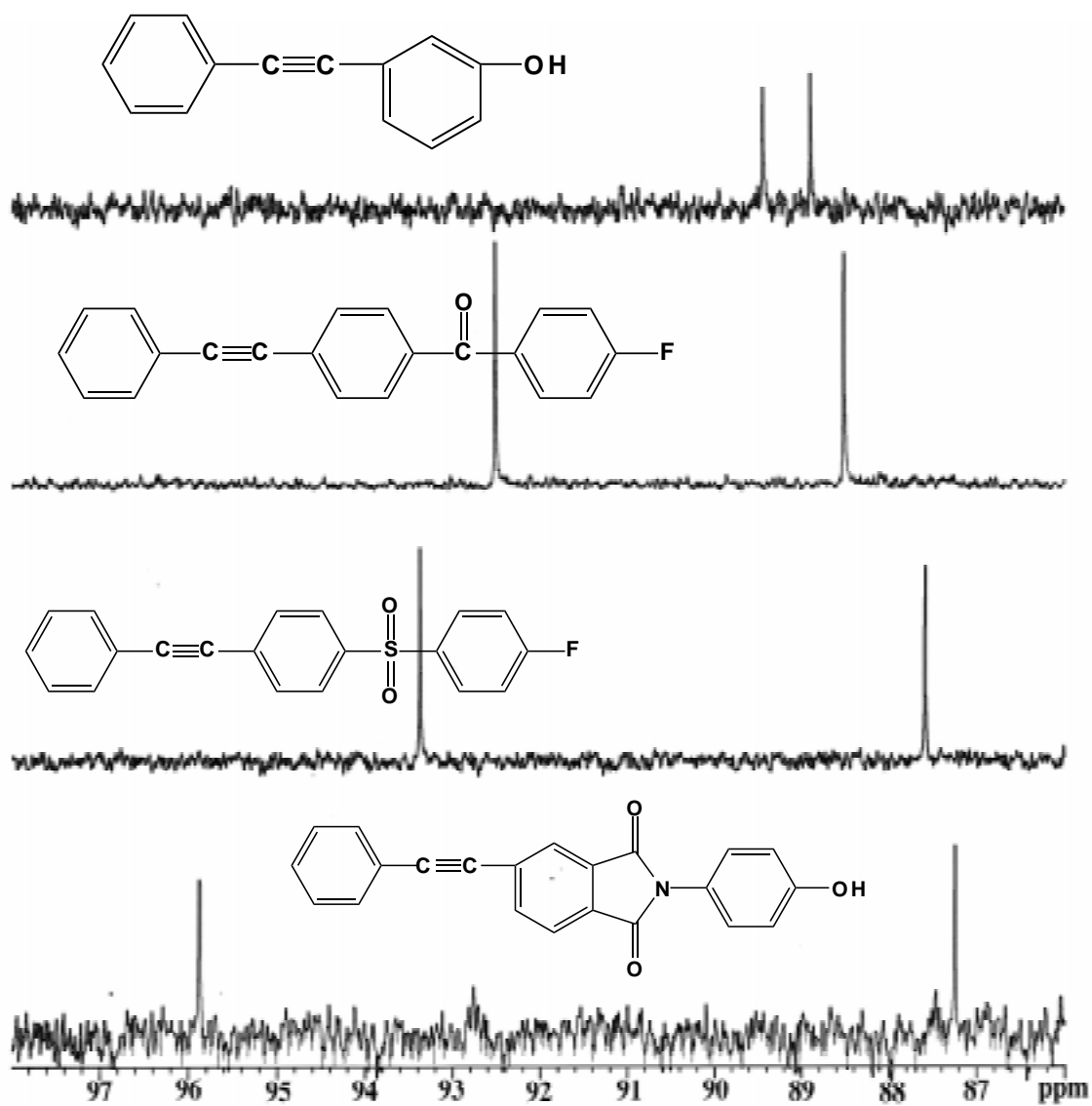


Figure 4.12 ^{13}C NMR of the Ethynyl Region of Phenylethynyl Monofunctional Endcappers

substituent. The trend for increasing polarizability corresponds with that of increasing electron affinity in the substituents indicating that this could indeed affect the reactivity of the ethynyl moiety.

All of the resonances of the ethynyl carbons of the endcappers are shifted downfield from the ethynyl carbon resonances in diphenylacetylene¹⁴⁴ indicating that there is greater electronic charge in the ethynyl carbons. As the electron affinity of the substituents increase so does the downfield shift and subsequently the electronic charge on the ethynyl carbons. The presence of this charge particularly on the C β carbon could affect the reactivity of the carbon during the curing reaction.

It should also be noted that the shifts of the aromatic protons appear to be affected by the changing substituents on the substituted ring. The protons are shifted downfield with increasing electron affinity of the substituent. This is true not only on the substituted ring but also on the unsubstituted ring, although to a somewhat smaller extent. The fact that there is any shift in the unsubstituted ring indicates that the electronic effect of the substituent is delocalized through the substituted ring and across the ethynyl moiety.

Table 4.1-¹³C Shift Values for Ethynyl Carbons in Diphenyl-acetylene Derivatives

Compound	Cα shift (ppm)	Cβ shift (ppm)	Cβ-Cα
Diphenylacetylene¹ 44	89.35	89.35	0
3-PEP	88.9	89.4	0.5
FPEB	88.5	92.5	4.0
PEFDPS	87.6	93.4	5.8
PEPIP	87.2	95.9	8.7

The mechanism of the thermal curing reaction of the phenylethynyl moiety remains obscure. Possibly by comparing curing kinetics and/or cured properties of polymers, such as the T_g , made with this series of endcappers some information about the mechanism of the cure could be elucidated and this work is continuing.

4.3 Molecular Weight and Endcapping of 3-Phenylethynylphenol

Terminated Oligomers

3-Phenylethynylphenol was used to control the molecular weight of a series of poly(arylene ether sulfone) oligomers, but more importantly, it allows for control of the endgroup structures of the oligomers. High gel fractions, which provide good chemical resistance, in the subsequently cured thermosets requires that both endgroups be able to react into the network. Therefore, essentially all of the oligomers must be difunctionally endcapped with phenylethynyl groups. Monitoring molecular weight control and endgroup control required two complementary characterization methods to be utilized. Thus, quantitative ^{13}C NMR was used as a method of endgroup analysis and GPC or size exclusion chromatography (SEC) was used in a quantitative way, with viscosity detectors and universal calibration to take into account hydrodynamic volume, as a method of molecular weight analysis.

4.3.1-Molecular Weight by Endgroup Analysis

^{13}C NMR spectra are shown for each type of polymer backbone with 3-phenylethynylphenol used as the endcapper, in figures 4.13, 4.14, 4.15 and 4.16. The peaks are labeled for each structure and there is no evidence for any other

endgroup structures than the phenylethynyl, within the sensitivity limits of the instrument.

The molecular weight was calculated from the ratio of the integration of a endgroup to that of the integration of a backbone carbon. This provides the number average number of repeat units. Multiplication of this number by the repeat unit molecular weight and addition of the endgroups mass provides the number average molecular weight (M_n).

As is evident from the spectra there is a great deal of error, on the order of $\pm 20\%$, in this method of analysis arising from the noise in the baseline and resolution of the peaks. The total acquisition time for each of the spectra shown varied from 90 minutes to 126 minutes. The number of scans for each spectrum varied because the scans were simply continued until the small ethynyl peaks were determined to be distinguishable from the baseline noise. The acquisition time (1.199 sec.) and relaxation delay (18.8 sec.) were held constant for all experiments. The other factor besides noise causing the integration values to be inaccurate is overlapping of peaks. There are many endcapper peaks which overlap with backbone peaks very slightly, making it difficult to measure the integrations of either peak well. It was found that some peaks were well resolved from other peaks, but due to baseline noise the integrations were slightly different, especially for the smaller endcapper peaks. Some of this error in the

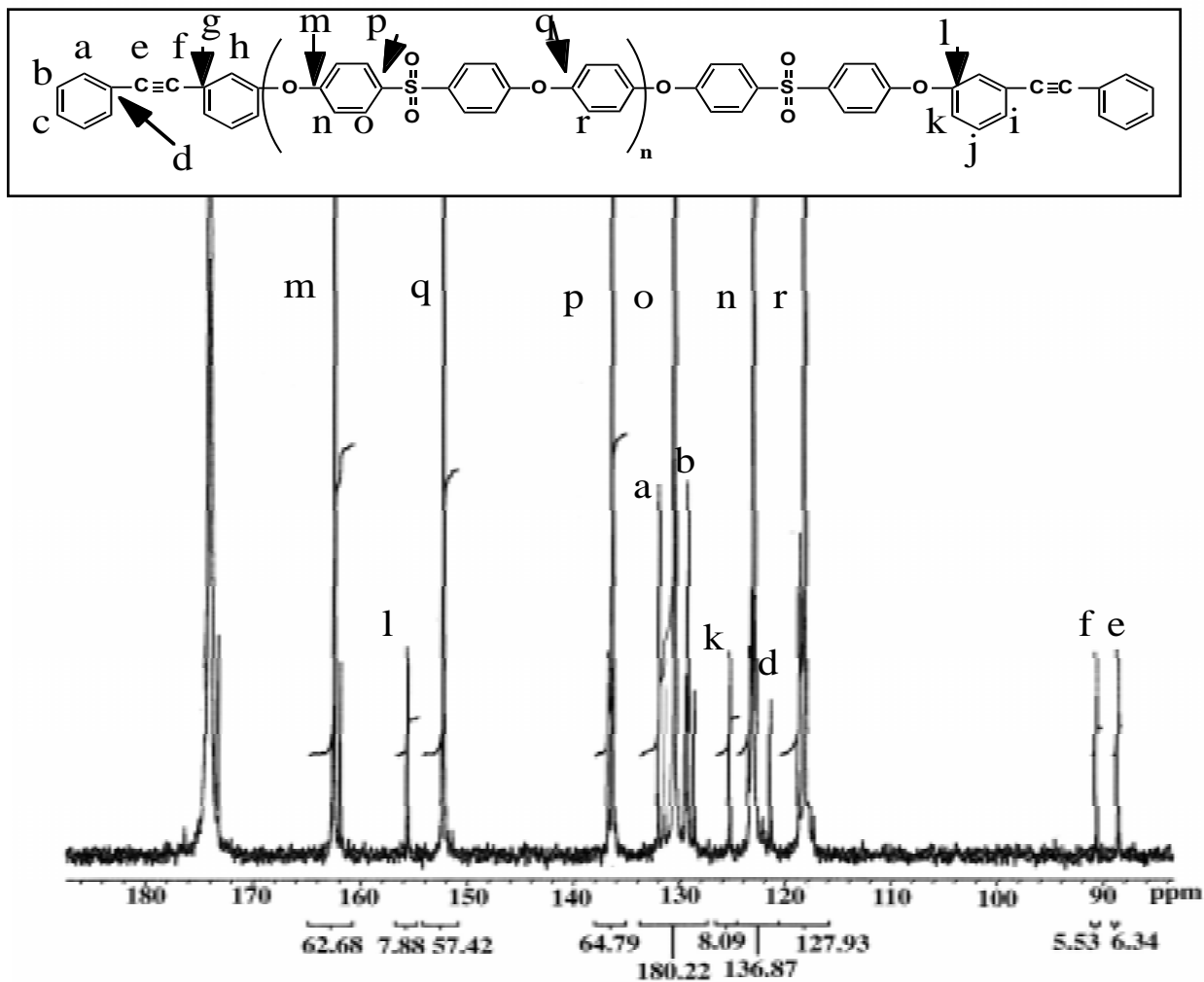


Figure 4.13 ^{13}C NMR Spectra of a 3,000 g/mole Phenylethynyl Terminated Hydroquinone Based Poly(arylene ether sulfone)

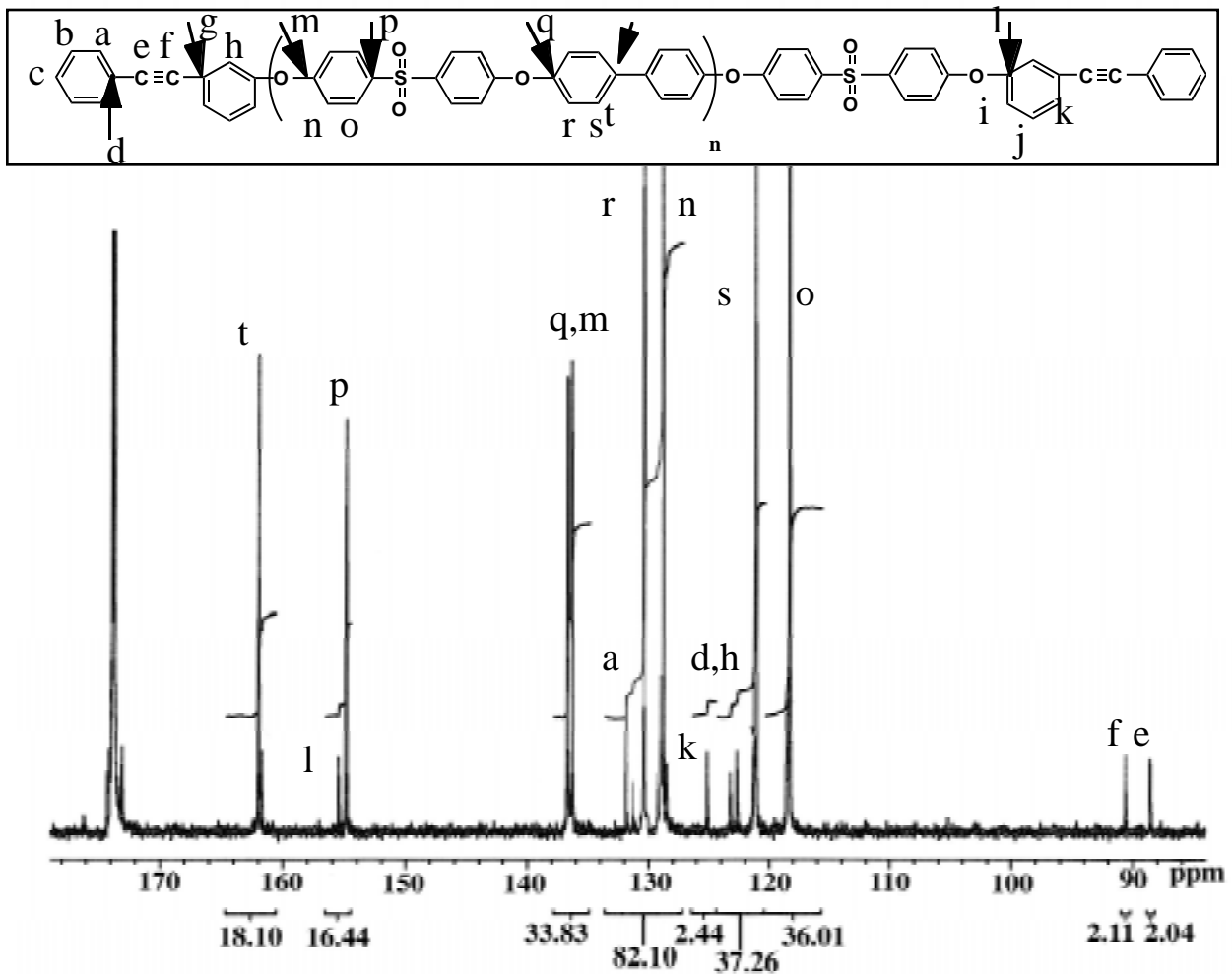


Figure 4.14 ^{13}C NMR Spectra of a 3,000 g/mole Phenylethynyl Terminated 4,4'-Biphenol Based Poly(arylene ether sulfone)

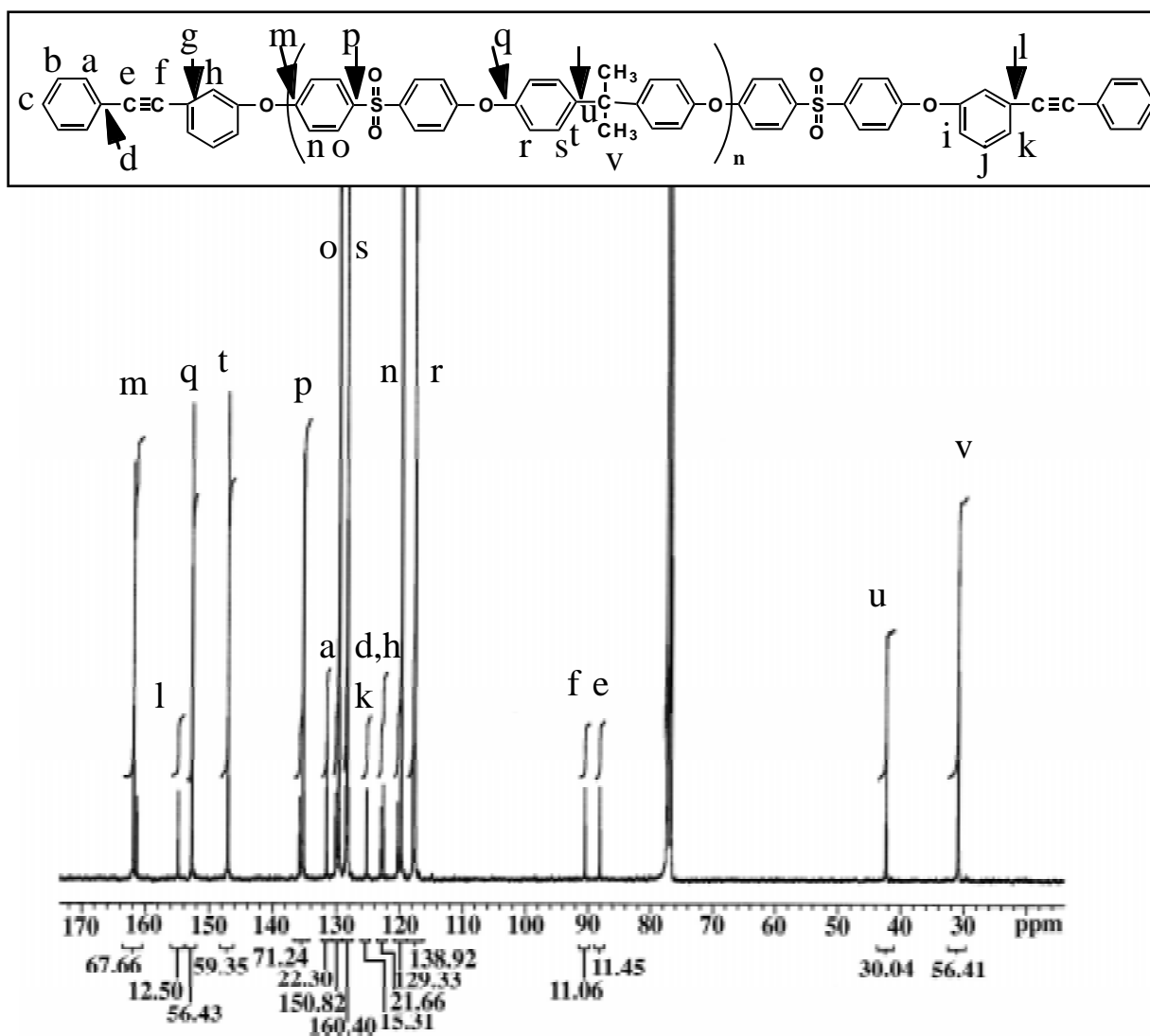


Figure 4.15 ^{13}C NMR Spectra of a 3,000 g/mole Phenylethynyl Terminated Bisphenol A Based Poly(arylene ether sulfone)

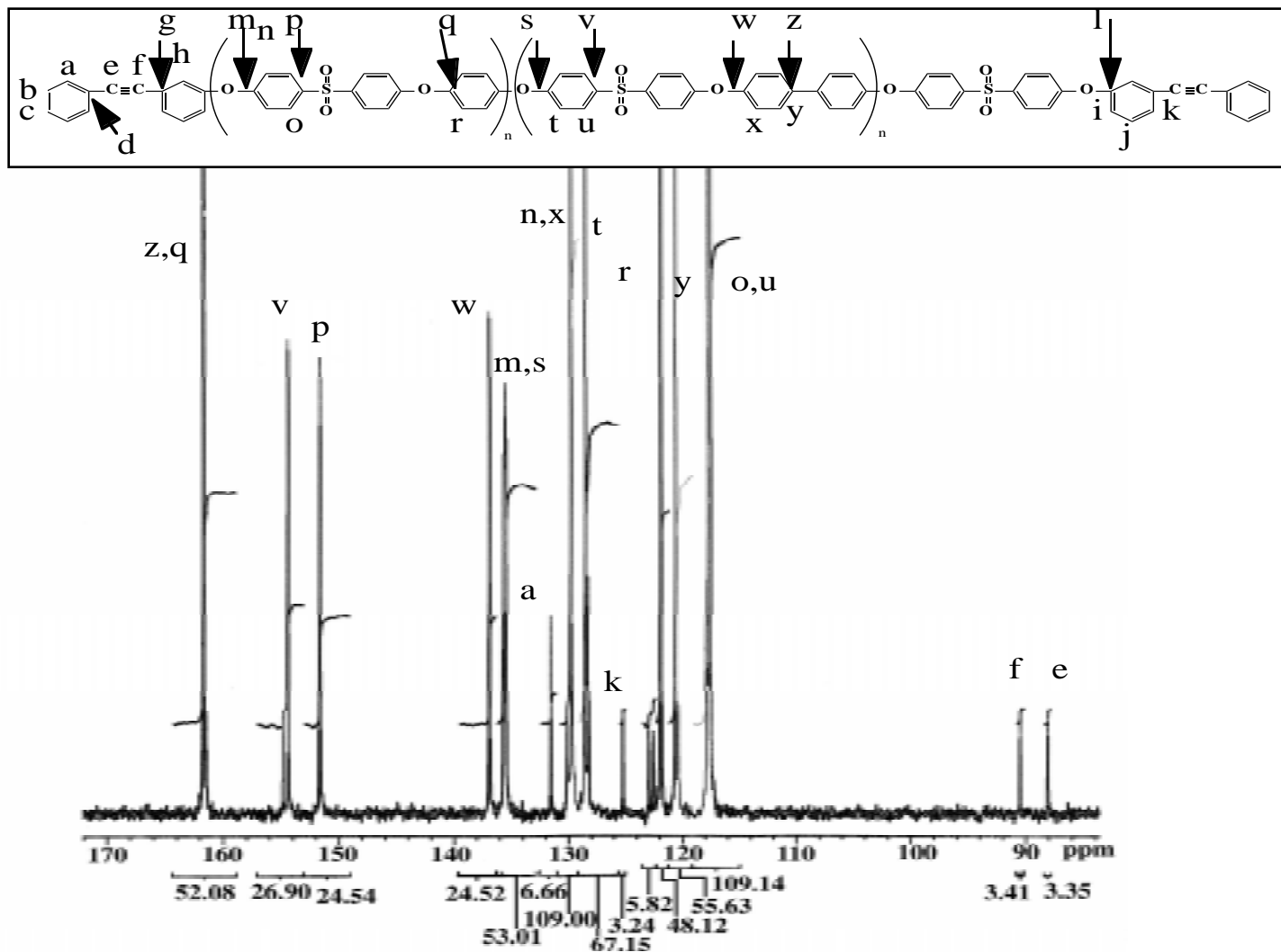


Figure 4.16 ^{13}C NMR Spectra of a 5,000 g/mole Phenylethynyl Terminated 50:50 Hydroquinone:4,4'-Biphenol Based Poly(arylene ether sulfone)

calculation of the M_n was overcome by taking an average for each spectrum. The integrations for the best resolved backbone and endcapper peaks were recorded and a M_n was calculated by ratioing each of the backbone peaks to each of the endcapper peaks. The average M_n was then derived from the average of these M_n values. The average values were calculated from a different total number of calculations for each system due to the slight differences in shifts causing overlapping to occur. The number of M_n values calculable from each spectrum ranged from as little as 6 to as many as 24. These average values are all shown in table 4.2.

The average values obtained for M_n were almost always higher than the targeted molecular. The discrepancy from the target M_n is present most likely due to two possible reasons. One reason for this could be inherent in the method of calculation used to make the controlled molecular weight oligomers. The calculations did take into account the endgroups, so that the molecular weight of the endgroups (about 603 g/mole) was subtracted from the target M_n initially. This new target M_n was then divided by the molecular weight of the repeat unit to obtain the average number of repeat units. The average number of repeat units was never a whole number whereas the actual number of repeat units is a whole number. For example in the calculations for the synthesis of a 5,000 g/mole hydroquinone based polymer endcapped with 3-PEP the first step was to subtract

Table 4.2 Average Mn values from ^{13}C NMR of 3-Phenylethynylphenol Terminated Oligomers

Bisphenol	Target M_n	NMR Avg. M_n
Hydroquinone	3,000	3,400 \pm 400
	5,000	5,500 \pm 750
4,4'-Biphenol	3,000	3,350 \pm 250
	5,000	5,300 \pm 400
Bisphenol A	3,000	2,850 \pm 150
	5,000	5,500 \pm 350
50 HQ/50 BP	5,000	6,200 \pm 200
60 HQ/40 BP	5,000	6,000 \pm 200
70 HQ/30 BP	5,000	6,100 \pm 600
80 HQ/ 20 BP	5,000	6,800 \pm 1000

the mass of the endgroups from the target molecular weight, providing a calculated target molecular weight of 4,397 g/mole. This was then divided by the mass of the repeat unit to provide a figure of 13.5559 average repeat units per polymer chain. Obviously, each polymer chain must have a whole number of repeat units so in the necessary addition of whole molecules the actual molecular weight of the individual oligomers will always be higher or lower than the target molecular weight by at least a small amount. It would be possible to do the calculations with whole repeat units to obtain a molecular weight that may be truer to the target molecular weight, which would not then be a rounded number. This exercise in precision would not necessarily give a number closer to the target molecular weight however because another important step that must be taken into account besides statistics is the work-up of the oligomers.

A statistical distribution of polymer chain sizes should be obtained with very few chains being extremely small and very few chains being quite large. As will be shown in the following section discussing the GPC results the molecular weight distribution is smaller than the expected one of 2.0 in all cases. This presents the likely possibility that one portion of the statistical chains are being lost. The most likely reason is that the very low molecular weight chains are soluble in methanol which is used to precipitate the oligomers after the polymerization is complete. Loss of the low molecular weight chains not only

narrows the molecular weight distribution, but increases the value of M_n concurrently. This would also explain why the experimentally measured molecular weights are slightly higher than the target molecular weights. The synthesis of controlled low molecular weight oligomers is more likely to lead to this development than high molecular weight polymers. The solubility of the low molecular weight chains remains constant for any given structure, but the fraction of chains which fall in this solubility range is greater for lower molecular weights, and thus the effect of their loss has more significance.

4.3.2 Molecular Weight by Size Exclusion Chromatography

Gel permeation chromatography (GPC) was conducted on the phenylethynyl terminated oligomers in either chloroform or NMP + P_2O_5 .^{136,137} Chloroform was used for the bisphenol A oligomers as well as for the chloroform soluble copolymers. In the other cases where the oligomers were not soluble in chloroform it was necessary to use NMP. The two solvents are run through different instruments in our laboratory but the detectors are essentially the same and the data obtained from both is considered to be of equal precision.

The data obtained from the GPC are in the form of raw chromatograms obtained from the two different detectors (figures 4.17 and 4.18), a calculated molecular weight distribution (figure 4.19) and calculated molecular weights.

The molecular weight distribution and numbers are obtained by numerical calculations from the data as described in Hiemenz.¹⁴⁵ The instrumental error for this type of characterization is on the order of 10%.¹⁴⁶ Possible sources of experimental error in the data are sample concentration deviations and baseline choice. The samples were dried, weighed and diluted very carefully, in order to minimize this type of error. The choice of baseline may not have remained entirely consistent as the calculations were performed in conjunction with two different colleagues (Dr. L. Dong and Dr. Q. Ji). The baseline choice becomes especially important in the low molecular weight region of the chromatogram, where a low molecular weight tail is observed in all cases. Thus, the degree of inclusion or exclusion of the low molecular weight tail can have a large effect on the M_n value as well as the M_w/M_n value.

The M_n , M_w and M_w/M_n values obtained for the phenylethynyl terminated oligomers from GPC measurements are shown in table 4.3. In most cases, as with the ^{13}C NMR results, the M_n values obtained are slightly higher than targeted M_n . The fact that both the GPC and ^{13}C NMR results have this same trend is good evidence that the actual M_n is slightly greater than the targeted molecular weight. Some possible reasons for this discrepancy were previously discussed in regards to the ^{13}C NMR data.

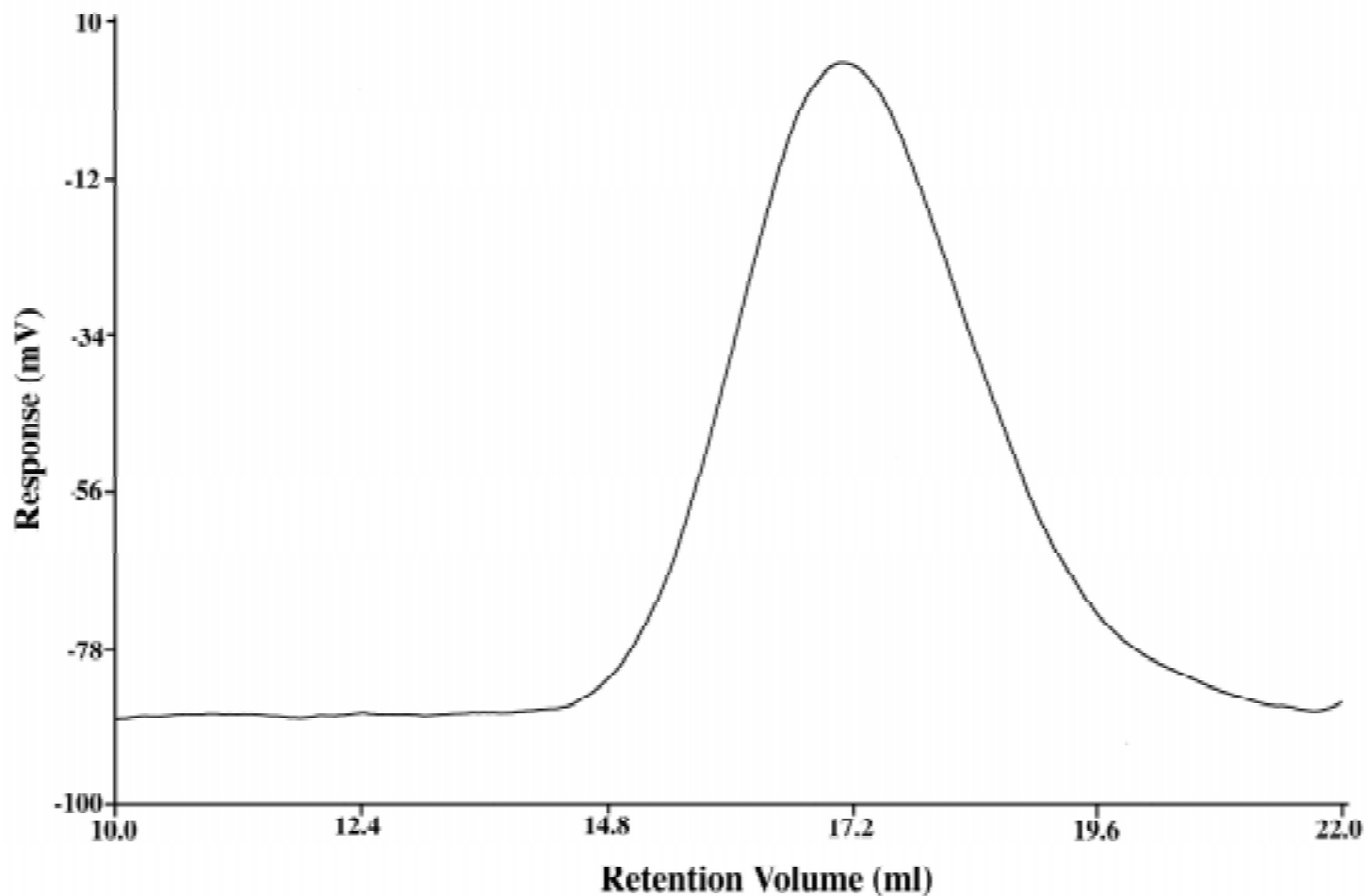


Figure 4.17 Size Exclusion Chromatogram (SEC) of a 5,000 g/mole Phenylethynyl Terminated 70:30 Hydroquinone:4,4'-Biphenol Poly(arylene ether sulfone) Copolymer Using a Differential Viscosity Detector

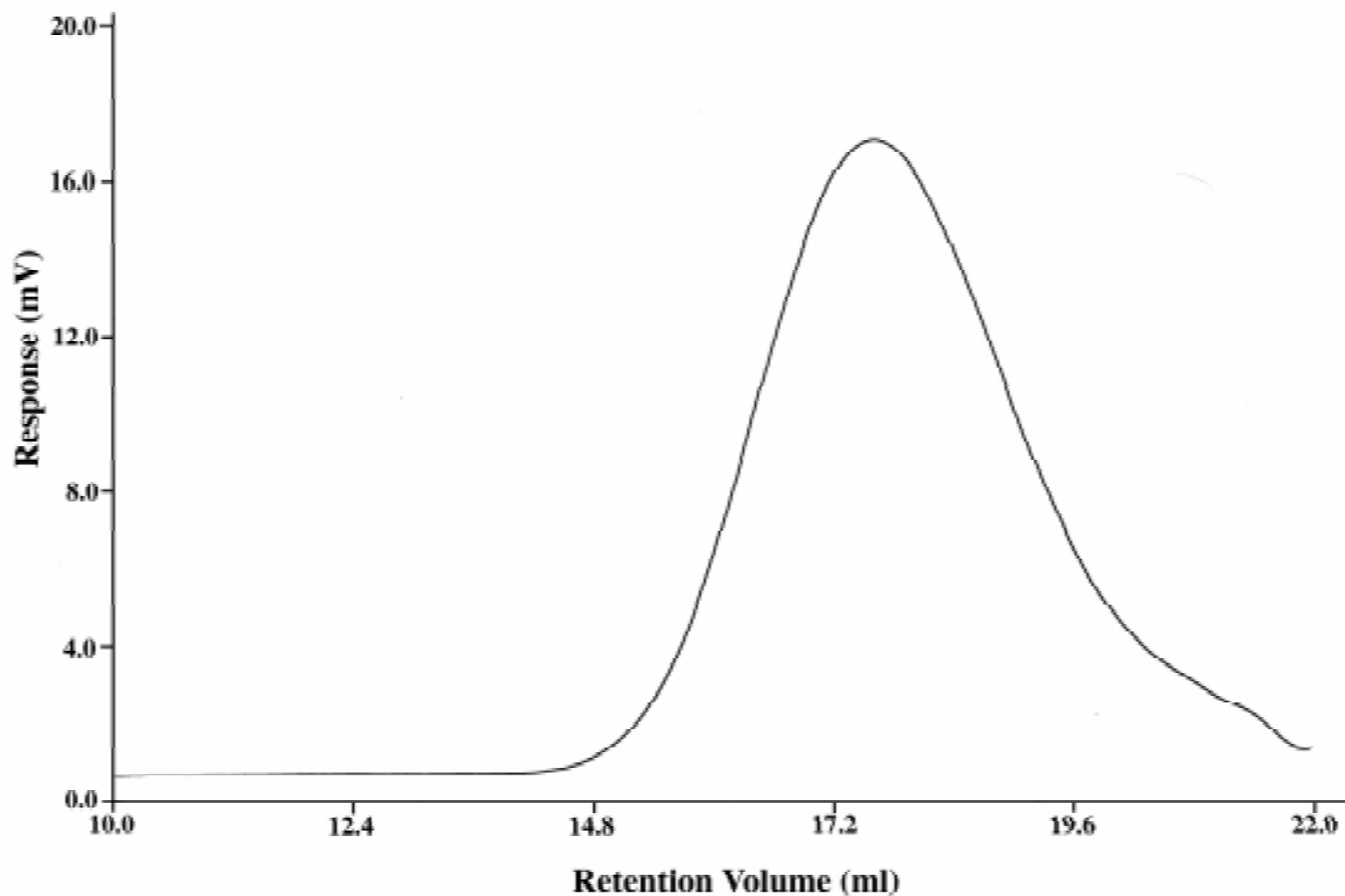


Figure 4.18 SEC of a 5,000 g/mole Phenylethynyl Terminated 70:30 Hydroquinone:4,4'-Biphenol Poly(arylene ether sulfone) Copolymer Using a Refractive Index Detector

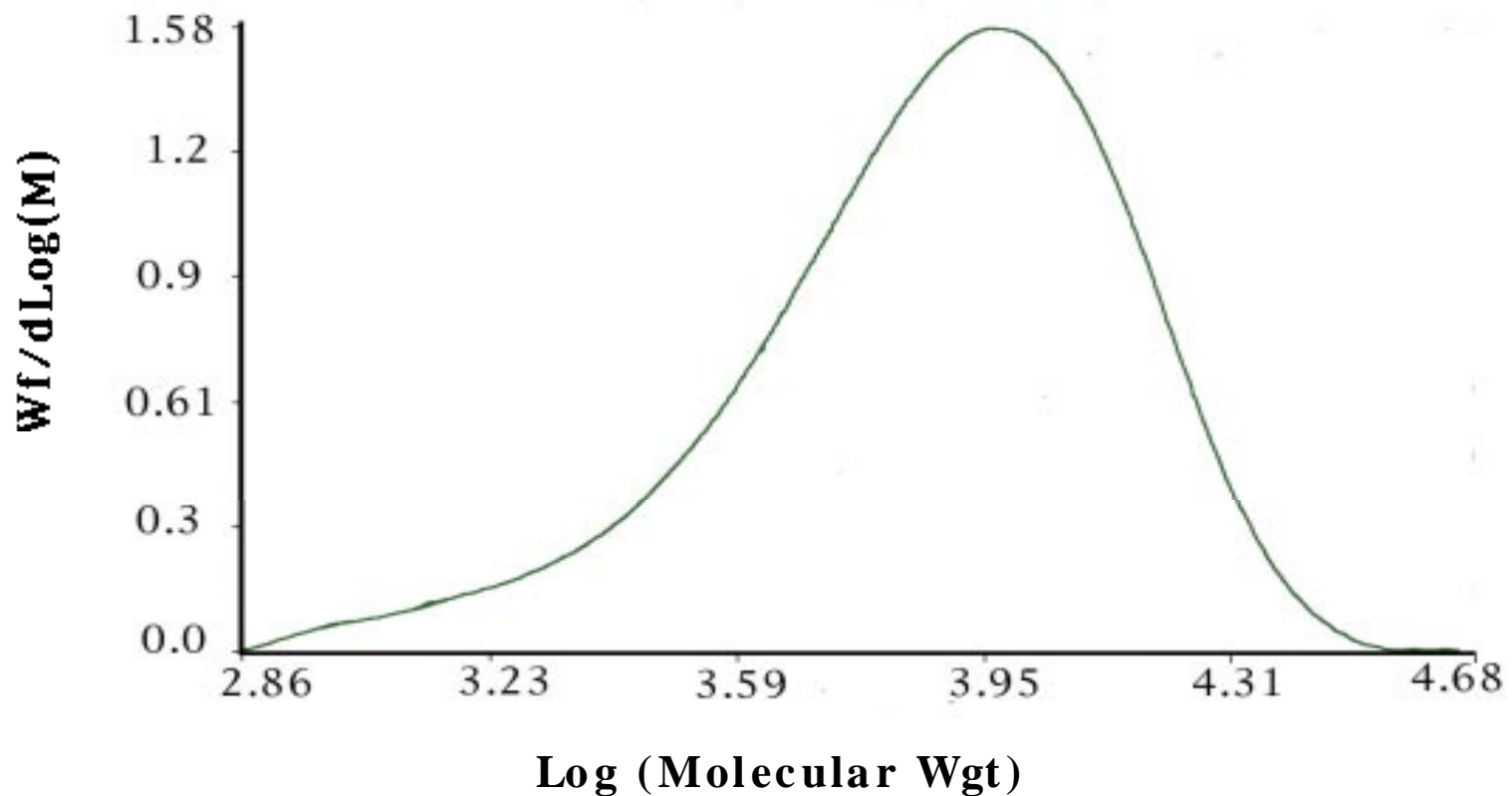


Figure 4.19 Molecular Weight Distribution of a 5,000 g/mole Phenylethynyl Terminated 70:30 Hydroquinone:4,4'-Biphenol Based Poly(arylene ether sulfone) Copolymer

The M_w/M_n values obtained by GPC measurement are almost all less than the expected value for a step-growth reaction of 2.0. In general the M_w/M_n values range from 1.5-1.8. This is with the exception of the 5,000 g/mole bisphenol A based oligomer. This is also the odd sample in terms of the M_n value. It is the only sample which shows a M_n less than the target M_n . This anomaly could be due to experimental error. Generally the GPC results appear to be consistent and, within error, they provide values very close to the target M_n and lower than the expected molecular weight distribution. When the equation $X_w/X_n = 1+p$ is used to calculate a molecular weight distribution for a 5,000 g/mole oligomer the expected value is 1.91 which is less than 2.0.¹³⁵ Another possible reason for a narrower distribution is that some of the lower molecular weight oligomers were likely removed from the distribution due to fractionation during the precipitation step of the workup procedure. Removal of this portion of the oligomers serves to increase the M_n and therefore narrow the molecular weight distribution.

Table 4.3 Calculated Molecular Weight Numbers from GPC for Phenylethynyl Terminated Poly(arylene ether sulfone) Oligomers

Bisphenol	Target M_n	M_n	M_w	M_w/M_n
Hydroquinone	3,000	3,120	4,940	1.58
	5,000	5,260	9,260	1.76
4,4'-Biphenol	3,000	3,280	5,260	1.60
	5,000	5,280	9,240	1.75
Bisphenol A	3,000	2,810	5,030	1.79
	5,000	4,510	9,820	2.18
50:50 HQ:BP	5,000	5,030	7,690	1.53
60:40 HQ:BP	5,000	5,820	8,900	1.53
70:30 HQ:BP	5,000	5,850	9,020	1.54
80:20 HQ:BP	5,000	5,720	8,720	1.52

4.3.3 Correlation of ^{13}C NMR and GPC Results

Correlation of the ^{13}C NMR results with the GPC results provides more information than just molecular weight. NMR alone is insufficient to provide definitive molecular weight data but it does provide structural information about the backbone of the polymer, as well as the endgroups if they are present in sufficient concentration. The integrations are a measure of the relative concentrations of particular carbon atoms in the sample. Use of the integrations to obtain the M_n of the sample requires an assumption that the sample is essentially quantitatively difunctionally terminated with the endgroup carbon used for the calculation. GPC is a definitive measurement of the size and, if properly calculated, molecular weight of the oligomer sample, but it does not provide any structural information such as the nature of the endgroups, or even of the backbone.

Utilization of these two methods of characterization provides good evidence that the materials are in fact quite efficiently difunctionally endcapped. If the M_n obtained from NMR and the M_n obtained from GPC are the same, then it follows that the material is in fact difunctionally endcapped. This is particularly important in the case of these thermosetting oligomers because in order for a high degree of cure to be attained it is necessary for essentially all of the oligomer chains to react into the network at both ends. Figure 4.20

graphically shows the correlation of the GPC data with the ^{13}C NMR data. The lines for the two methods are fairly close with similar slopes of 1.14 for the GPC data, 1.29 for the NMR data and correlation coefficients of 0.995 for both lines. This correlation indicates that the endgroup control with 3-phenylethynylphenol is good.

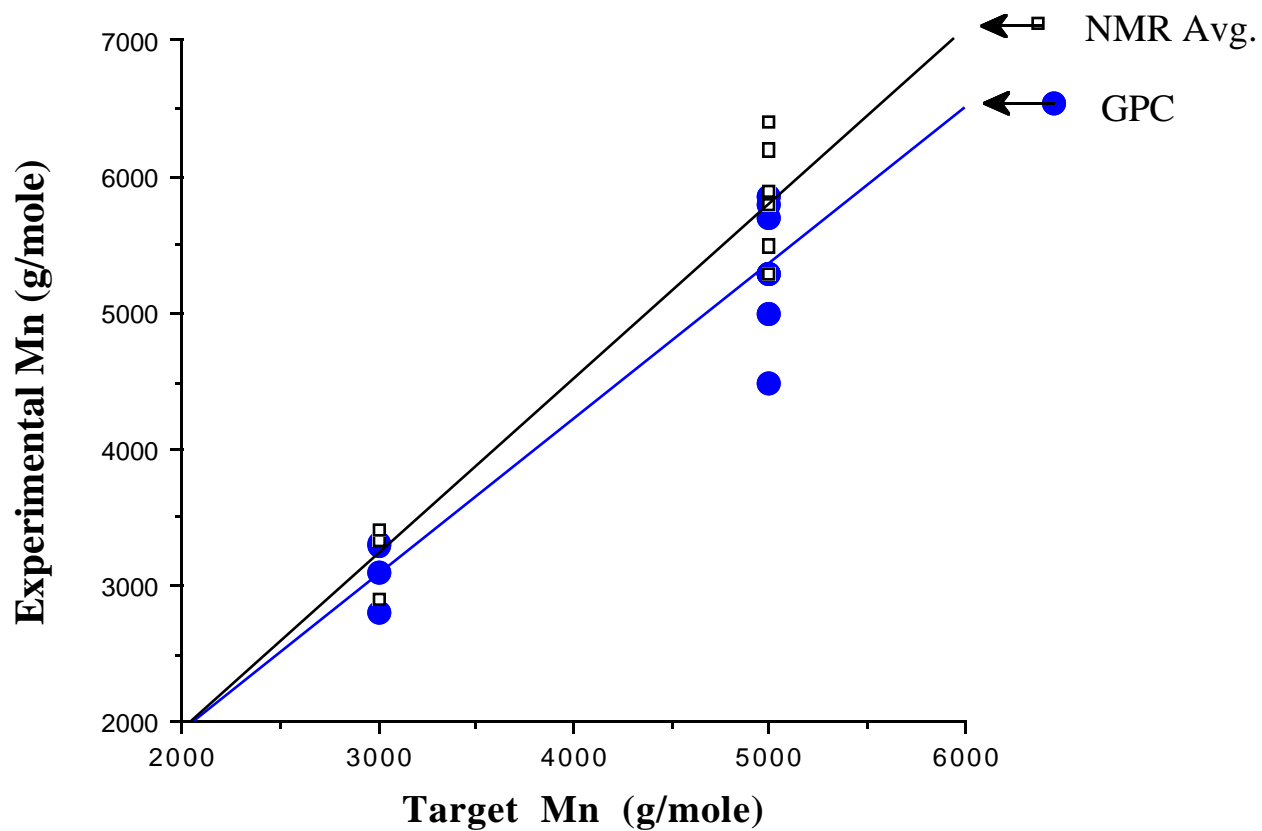


Figure 4.20 Experimental M_n vs. Target M_n for a Series of Phenylethynyl Terminated Poly(arylene ether sulfone) Oligomers

4.4 Curing of Phenylethynyl Oligomers: Network Formation

The mechanism of the curing reaction of the phenylethynyl moiety has not yet been well elucidated but it is evident that the thermally initiated reaction occurs at an appreciable rate only at very high temperatures, e.g. $> 350^{\circ}\text{C}$. This section will cover the investigation of the processing conditions necessary to cure the phenylethynyl terminated oligomers. Firstly, the melt rheology data will be presented and discussed and then the gel fraction studies will be reported.

4.4.1 Rheology

Initial studies to determine the approximate onset of cure of the phenylethynyl terminated oligomers were conducted with Bohlin VOR parallel plate melt rheometer. Control of atmosphere and temperature are possible when measurements are taken in the oscillation mode with this instrument. ^{62,141,142} The oligomers measured for this study were a 5,000 g/mole hydroquinone based and a 2,000 g/mole bisphenol A based oligomer. The first measurements were done in a dynamic temperature mode in which the melt viscosity was measured vs. temperature. The dynamic temperature curves are given in figures 4.21 and 4.22.

The hydroquinone based oligomer shows a dramatic drop in the melt viscosity at around 300°C . As will be discussed later, in section 4.5.2 on the

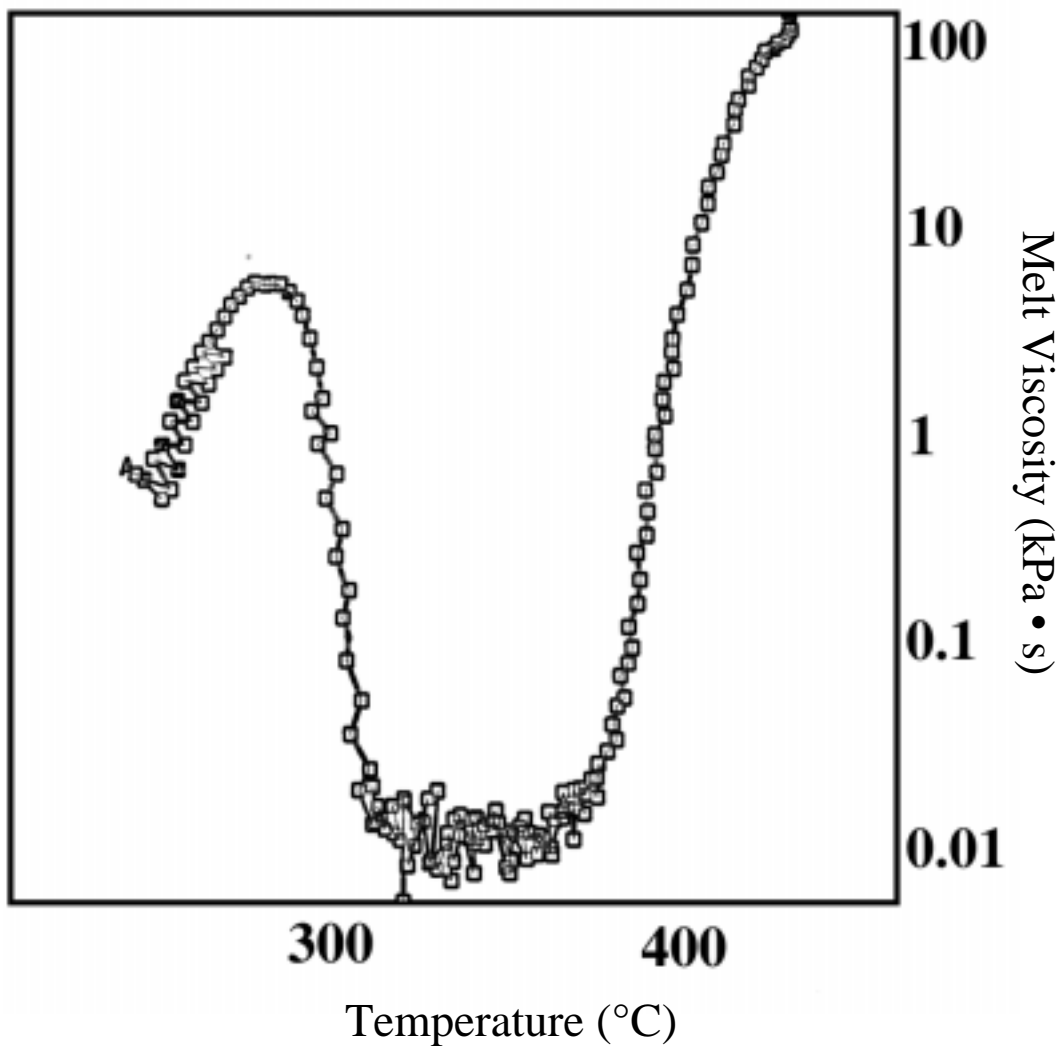
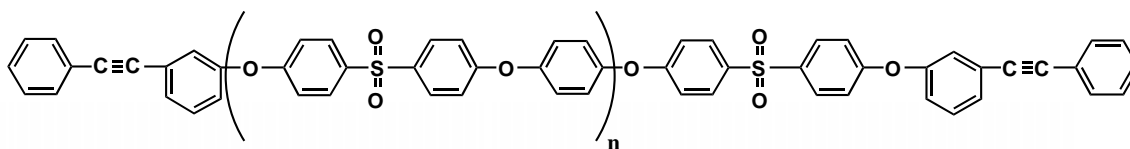


Figure 4.21 Melt Viscosity vs. Temperature for a 5,000 g/mole Phenylethynyl Terminated Poly(arylene ether sulfone) at a Heating Rate of 3°C/min.

thermal transition of oligomers, some of these poly(arylene ether sulfone) oligomers are able to crystallize from solvent but not from the melt. Thus, after the initial workup of the oligomers from solvent a melting transition is seen due to melting of the semi-crystalline regions. The temperature at which this dramatic drop in viscosity occurs corresponds closely with the T_m of the crystalline regions in the solvent crystallized hydroquinone based oligomer. There is a low viscosity region from around 300-380°C. The low viscosity region is noisy because the instrument is unable to measure these very low viscosities. Although a good measure of the minimum viscosity from this curve is not possible, there is a dramatic increase in the melt viscosity which appears to occur at about 380°C, signaling the gel point and the initial network formation.

Figure 4.22 shows the melt rheology of the 2,000 g/mole phenylethynyl terminated bisphenol A based system. The drop in viscosity for this amorphous oligomer is not so dramatic as with the semicrystalline oligomer and occurs immediately after the oligomer passes through its glass transition temperature (T_g). The low viscosity temperature interval is much larger and extends from around 200-380°C. The minimum viscosity region appears to show even more scatter than was present in the hydroquinone based system. Again, pinpointing a number for the minimum viscosity is not possible with this experiment. The

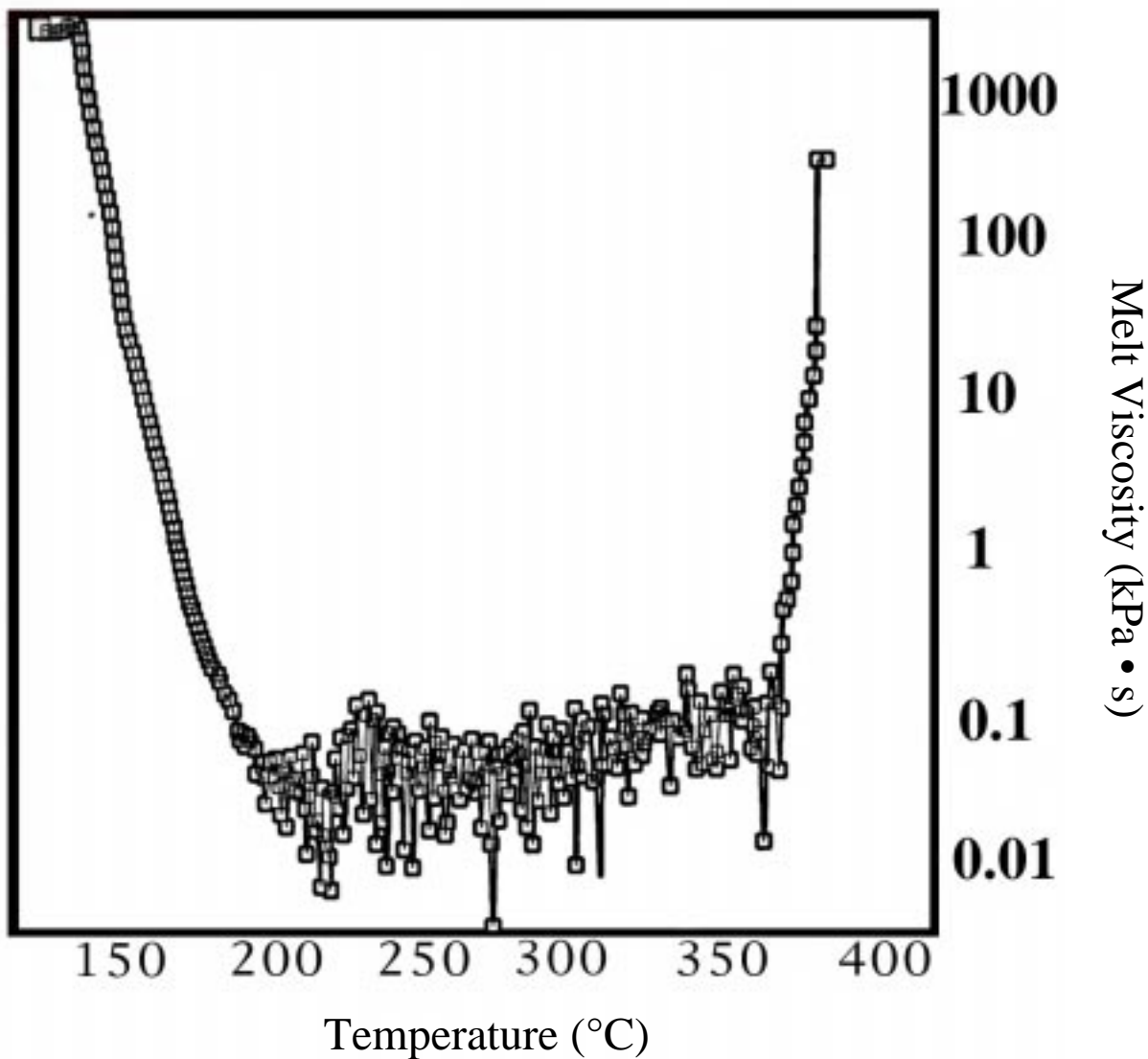
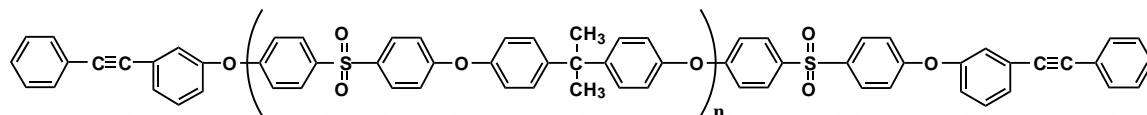


Figure 4.22 Melt Viscosity vs. Temperature for a 2,000 g/mole Phenylethynyl Terminated Poly(ether sulfone) at a Heating Rate of 3°C/min.

heating rates were the same for the two oligomers and the onset of cure appears to occur at the same temperature even though the processing window for the bisphenol A based oligomer is much larger.

This brings us to the question of what temperature is optimum for processing and curing of these materials. Isothermal experiments at two different temperatures were conducted on the hydroquinone based system to obtain a qualitative comparison of the curing rate at different temperatures. The results of these measurements are given in figure 4.23. The increase in viscosity with time under isothermal conditions is very different at 350°C as compared to the increase at 380°C. At 350°C it takes about 25 minutes to reach a melt viscosity of 40 kPas. At 380°C it takes only about 10 minutes to reach the same viscosity. In these initial stages it is reasonable to equate the melt viscosity with the degree of cure or with the average molecular weight. At low molecular weights, essentially below entanglement length for linear polymers, the melt viscosity should scale linearly with molecular weight. At higher molecular weights the melt viscosity should scale to the 3.4 power of molecular weight. Again, this is for linear polymers which is a much less complicated situation than for network structures. The increase in viscosity with time does indicate that curing is taking place that is increasing the molecular weight of the sample. It was necessary to stop the experiment before the viscosity became too high and before the sample cured to

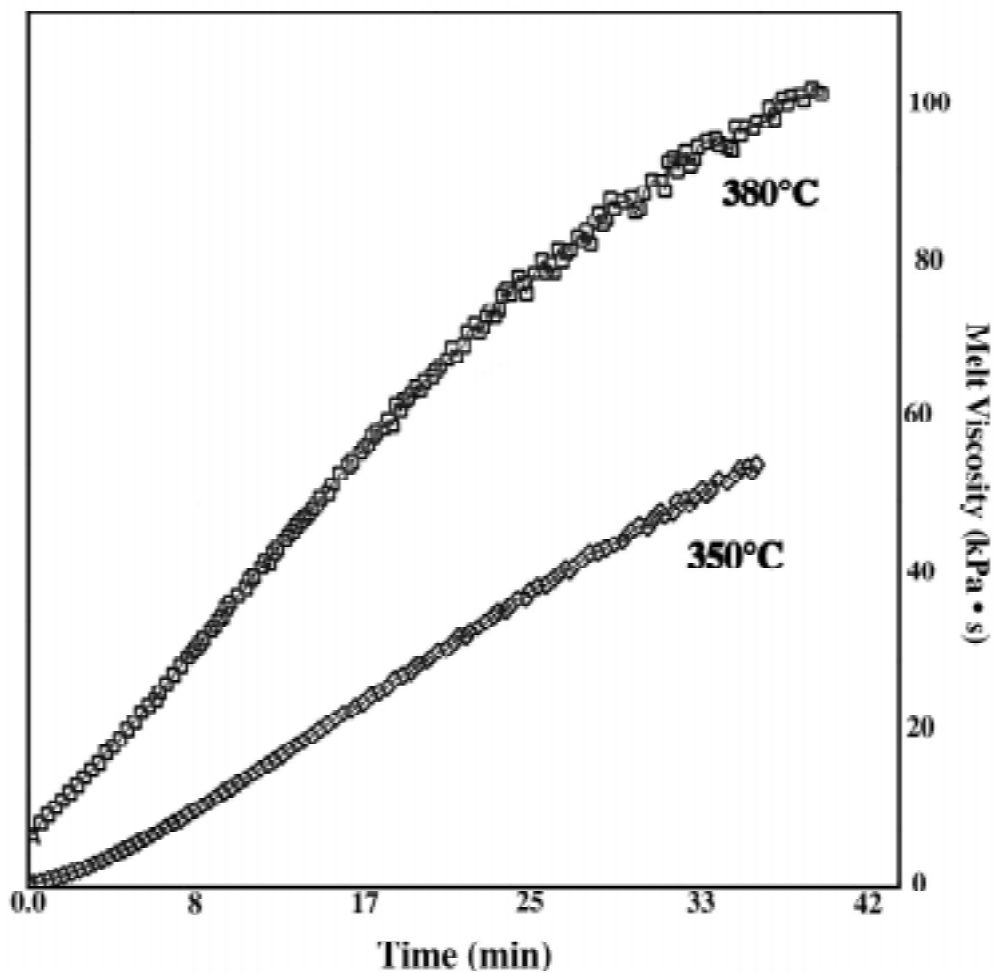
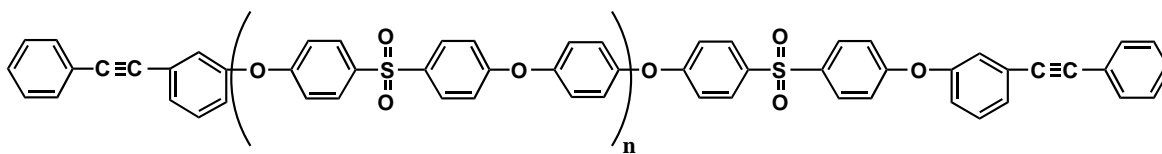


Figure 4.23 Melt Viscosity vs. Time for a 5,000 g/mole Phenylethynyl Terminated Poly(arylene ether sulfone) Under Isothermal Conditions of 350°C and 380°C.

such an extent as to glue the parallel plates together permanently. We would expect to eventually see a dramatic increase in the viscosity as the material became fully gelled.

4.4.2 Extent of Cure

The curing reaction leading to a network clearly takes place at temperatures in the range of 350°C-380°C or higher and the reaction is clearly faster at higher temperatures. It was necessary to determine the curing conditions necessary to achieve a fully cured high gel fraction thermoset before undertaking studies to measure the adhesive properties of the thermosets. Samples were cured by various methods throughout this research. Many samples were cured in a closed mold at 370°C. The gel fractions for some of these samples are given in Table 4.4. There were also many attempts to simply cure samples in a convection oven, under either a nitrogen or air atmosphere. However, there was much inconsistency in this later data, probably due to poor temperature control in the oven. In addition, some samples were cured directly in the DSC. These samples were suitable for obtaining T_g values but were too small for gel fraction studies. An additional set of samples was also cured in the press to produce the single lap shear samples. These samples were also unsuitable for obtaining gel fractions, since they were intimately combined with the scrim

Table 4.4 Gel Fraction of Cured Poly(arylene ether sulfone) Oligomers from Soxhlet Extraction with Chloroform for 4 Days.

Polymer	Target Mn (g/mole)	Cure Temp. (°C)	Cure Time (min)	% Gel (% gel of different film)
Bisphenol A	2,000	370	90	93
	3,000	370	90	78
	5,000	370	90	91
Hydroquinone	3,000	370	90	97 (94)
	5,000	370	90	93
4,4'-Biphenol	3,000	370	90	86 (61)
	5,000	370	120	90 (91)
50:50 HQ:BP	5,000	370	120	90

glass fabric.

Table 4.4 lists the gel fractions as a function of cure time and temperature. These values were obtained from multiple Soxhlet samples on compression molded films. In all cases the discrepancy between films was no more than 2% and in most cases the discrepancy was less than 0.5%. The gel fractions obtained at 370°C for 90 minutes are very good in most cases. The 4,4'-biphenol system appears to require a longer cure time in order to reach higher gel fractions, perhaps reflecting its stiffer chain. For this reason the copolymers were cured under the extended time conditions in the preparation of the single lap shear samples. The films were all molded at Virginia Tech with the help of Dr. Venkat Vasudevan except for four films which were pressed in the labs of Prof. Tae-Ho Yoon in the Department of Materials Science and Engineering at Kwang Ju University in Kwang Ju, Korea. The three % gel values in parentheses are data from three of the films as well as the 5,000 g/mole hydroquinone based sample. In all three cases where two films were produced, the materials were the same oligomer batch and the curing conditions were essentially the same. Heating and cooling cycles and/or temperature control could have differed which may account for the discrepancies. In general the gel fractions obtained from this study are high and indicate that the materials are essentially fully cured. This is more important, though indirect, evidence that the oligomers are fully endcapped.

4.5 Thermal Analysis of Oligomers and Thermosets

This section describes the thermal behavior of the series of phenylethynyl terminated poly(arylene ether sulfone) oligomers synthesized with 3-phenylethynylphenol. It should be pointed out that these materials were designed to be useful as structural adhesives for aerospace applications where the use temperature is projected to be 177-204°C for up to 60,000 hours.⁸⁶ The applicability of these materials for this type of application will be discussed.

4.5.1 Thermal Stability

It has been shown in the previous section that curing of these materials must be carried out at very high temperatures. The actual minimum temperature at which the curing reaction will occur has not been determined but it clearly takes place at a much slower rate when the temperature is decreased. To obtain a high gel fraction in an appreciable time period of 90-120 minutes it is necessary to conduct the curing reaction at 370°C. The thermal stability of the material is obviously important at this temperature. For example, if degradation of the material were to occur at the curing temperature, then the integrity of the structural bond would of course be in question.

Figure 4.24 shows the dynamic thermogravimetric analysis of each backbone structure employed. The samples were examined as uncured oligomers

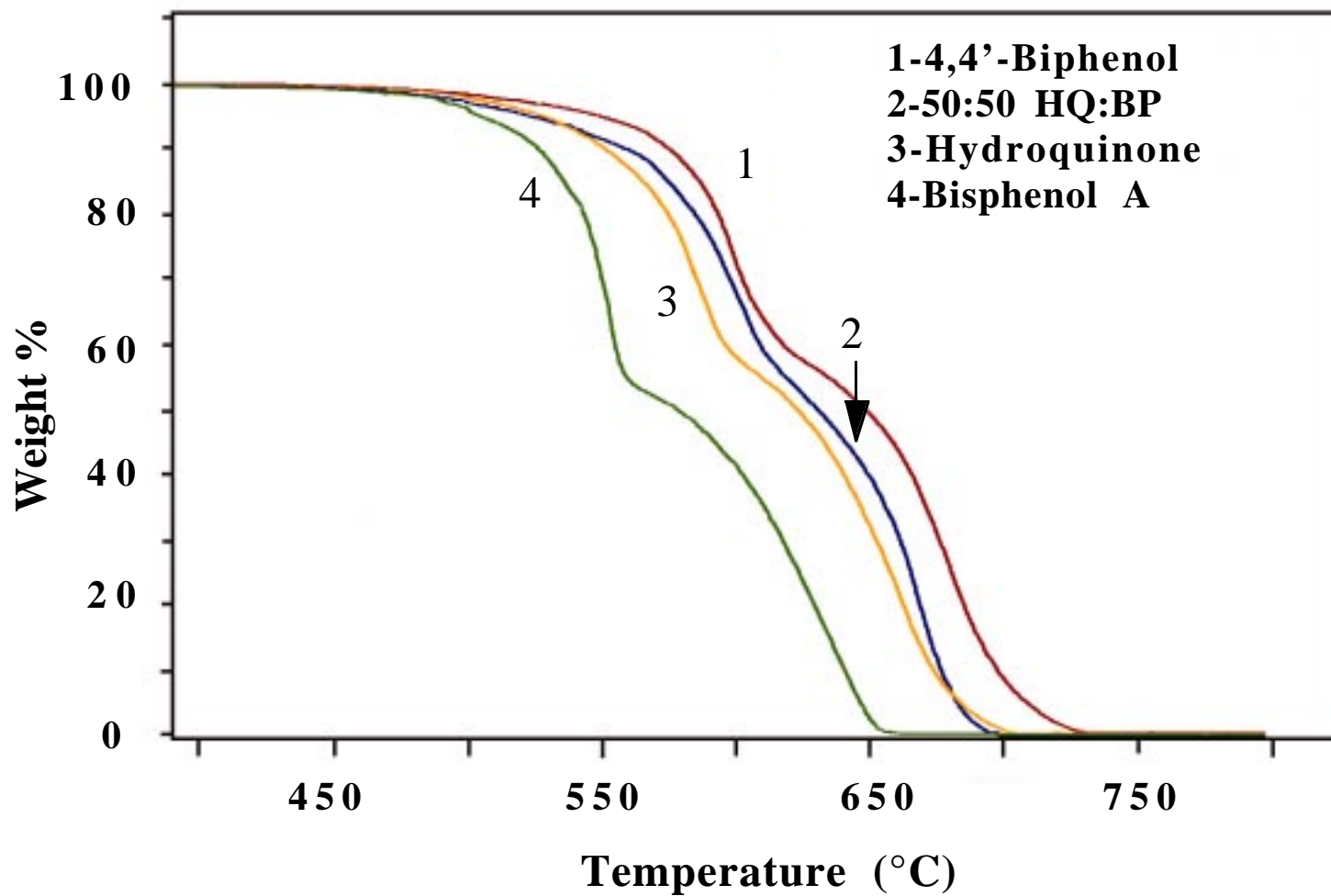


Figure 4.24 Thermogravimetric Analysis of Uncured 5,000 g/mole Phenylethynyl Terminated Poly(arylene ether sulfone) Oligomers Based on Different Bisphenols at 10°C/min in Air

in the form of a powder. All of the other samples behaved similarly to those provided as examples. The samples all retained their weight until the onset of degradation where a precipitous drop in weight occurred corresponding to major thermal fragmentation of the materials. The structural differences in the materials did produce slightly different degradation behavior and the most obvious example is the bisphenol A based system. The presence of the aliphatic isopropylidene in the bisphenol A results in a reduced 5% weight loss value for this structure. The weight loss profile appears identical to its more stable counterparts but the temperatures are reduced.

The temperatures at which 5% of the weight has been lost for all of the oligomers are provided in table 4.5. These samples were all initially uncured which may explain why there may be some modest molecular weight dependence at least for the hydroquinone and biphenol based systems.

Imparting more aromatic character to the backbone structure increases the thermal stability as is shown by the increased stability of the biphenol system over the hydroquinone system. The copolymers possess intermediate thermal stability between the hydroquinone and biphenol systems which is as expected for a random or statistical copolymer.

The aliphatic containing bisphenol A system shows slightly reduced thermal stability from the all aromatic systems, however its thermal stability is still

in the form of a powder. All of the other samples behaved similarly to those provided as examples. The samples all retained their weight until the onset of degradation where a precipitous drop in weight occurred corresponding to major thermal fragmentation of the materials. The structural differences in the materials did produce slightly different degradation behavior and the most obvious example is the bisphenol A based system. The presence of the aliphatic isopropylidene in the bisphenol A results in a reduced 5% weight loss value for this structure. The weight loss profile appears identical to its more stable counterparts but the temperatures are reduced.

The temperatures at which 5% of the weight has been lost for all of the oligomers are provided in table 4.5. These samples were all initially uncured which may explain why there may be some modest molecular weight dependence at least for the hydroquinone and biphenol based systems.

Imparting more aromatic character to the backbone structure increases the thermal stability as is shown by the increased stability of the biphenol system over the hydroquinone system. The copolymers possess intermediate thermal stability between the hydroquinone and biphenol systems which is as expected for a random or statistical copolymer.

The aliphatic containing bisphenol A system shows slightly reduced thermal stability from the all aromatic systems, however its thermal stability is still

Table 4.5 5% Weight Loss for Phenylethynyl Terminated Poly(arylene ether sulfone) Oligomers Measured from TGA at 10°C/min.

Bisphenol	Target Mn	Temp. at 5% Wgt. Loss (°C)
Bisphenol A	2,000	506
	3,000	501
	5,000	504
Hydroquinone	3,000	513
	5,000	527
Biphenol	3,000	534
	5,000	549
50:50 HQ:BP	5,000	523
60:40 HQ:BP	5,000	528
70:30 HQ:BP	5,000	531
80:20 HQ:BP	5,000	531

excellent at the curing temperature of 370°C under the dynamic conditions of this experiment. Isothermal experiments with these materials were also conducted at 370°C for 120 minutes. No weight loss was measured by the TGA and no exothermic or endothermic degradative behavior was observed in the DSC.

4.5.2 Thermal Transitions of Oligomers

The glass transition temperatures of the uncured oligomeric materials were measured by differential scanning calorimetry (DSC) from the second heat at a heating rate of 10°C/min. The melting transition temperatures were measured from the first heat of the DSC. It was very important not to heat these thermally reactive oligomers to a temperature where curing took place in the first heat. This was easily accomplished for the fully amorphous material but the semi-crystalline materials, particularly the hydroquinone based system, had to be heated to above 310°C to melt all of the solvent induced crystals. The sample was then quench cooled so it is very unlikely that any appreciable amount of cure could have taken place at that temperature for such a short time.

Glass Transition Temperatures

The thermal transitions of the 3-phenylethynylphenol terminated oligomers are provided in table 4.6. All of the different systems show an increase in T_g

Table 4.6 Thermal Transition Temperatures of Phenylethynyl Terminated Poly(arylene ether sulfone) Oligomers from DSC at 10°C/min.

Bisphenol	Target Mn (g/mole)	T_g (°C)	T_m(°C)
Bisphenol A	2,000	122	NA
	3,000	139	NA
	5,000	153	NA
Hydroquinone	3,000	155	300 (broad)
	5,000	173	300 (broad)
4,4'-Biphenol	3,000	166	NO
	5,000	184	NO
50:50 HQ:BP	5,000	173	NA
60:40 HQ:BP	5,000	165	NA
70:30 HQ:BP	5,000	173	240 (broad)
80:20 HQ:BP	5,000	180	253 (broad)

with molecular weight of the oligomer indicating that the number of chain ends is still high and the molecular weights are still in the range below the entanglement molecular weight where the properties are largely molecular weight dependent. There is a trend in the glass transition temperatures which corresponds to molecular structure as well. Thus, the bisphenol A system has the lowest T_g s while the hydroquinone is intermediate and the 4,4'-biphenol T_g s are highest.

This brings us to a discussion of why the copolymer system was developed. The amorphous bisphenol A system has some advantages in processing over the semi-crystalline hydroquinone and biphenol systems. This was demonstrated in the rheology studies, where the expanded low viscosity temperature range of the bisphenol A oligomer was observed. Elimination of the semi-crystalline regions allows the material to flow at temperatures just above the oligomeric glass transition temperature. The glass transition temperatures for the bisphenol A system are likely to be too low for the intended aerospace structural adhesive applications. However, the hydroquinone and particularly the biphenol systems have a much better chance of ultimately obtaining cured glass transition temperatures in the region needed for these high temperature applications. Synthesis of random copolymers of hydroquinone and 4,4'-biphenol was undertaken in order to produce amorphous materials, possessing large processing

windows, which still might have cured glass transition temperatures high enough for aerospace applications.

The T_g values for the wholly aromatic copolymers are higher than for the bisphenol A based materials, as anticipated. The T_g s are similar to the hydroquinone based materials, but do not exhibit a clear trend with comonomer composition. This behavior was observed with the analogous high molecular weight copolymers synthesized by Hedrick et. al.⁶ as well. However, the 50% and 60% hydroquinone containing copolymers are amorphous and should show an extensive processing window of about 150°C. The 70% and 80% hydroquinone containing copolymers are not amorphous but still should have a larger processing window than either of the respective homopolymers.

Melting Transition Temperatures

The column in table 4.6 providing melting transition temperatures is of course not applicable (NA) for the amorphous, soluble systems. The melting endotherms observed for the hydroquinone based system were small and broad. No visible melting transitions were observed for the 4,4'-biphenol based systems even though there is other evidence (e.g. solvent resistance) to indicate some ordered regions could be present. The biphenol based oligomers are insoluble in chloroform and also show poor flow properties even at 250°C which is well

above the glass transition temperatures of the low molecular weight oligomers. It is important to note also that these materials are semi-crystalline only after exposure to solvent. In other words they can kinetically crystallize from solvent but not from the melt, possibly related to T_g depression in the presence of the organic liquid. Once they have passed through the melting transition they do not recrystallize and are wholly amorphous materials.

The observed melting transitions for the semi-crystalline copolymers are somewhat surprising. High molecular weight thermoplastic versions of these same copolymer compositions were reported previously by Hedrick et. al.⁶ and were soluble in chloroform and wholly amorphous. The 70 and 80 weight % hydroquinone containing copolymers of 5,000 g/mole endcapped with 3-phenylethynylphenol are insoluble in chloroform and show melting transitions in the temperature range below that of the hydroquinone copolymer. When the amount of comonomer, 4,4'-biphenol was increased a decreased melting transition temperature was observed, particularly in the 20% and 30% biphenol containing copolymers. A further increase in the amount of 4,4'-biphenol to 40% results in a wholly amorphous. Figure 4.25 shows three DSC thermograms; the top curve is the 5,000 g/mole hydroquinone homopolymer and the semi-crystalline copolymer curves are shown below the homopolymer. The heats of fusion calculated from the area under the melting transition peak are given in

table 4.7. Typically the heat of fusion decreases with random copolymers, as is observed for this system. As was previously mentioned, the semicrystallinity only develops in solution and does not reappear after heating above T_m . It was found that the workup conditions (e.g. solvent/nonsolvent concentrations, etc.) for the polymers could have a large effect on the rate of crystallization and this may have induced different amounts of crystallization in solution. In order to obtain consistent results for the calculation of the heat of fusion, all three semicrystalline oligomers were reprecipitated under the same conditions from a dilute NMP solution into a stirred large volume of methanol. The samples were all dried under similar conditions in a vacuum oven at 195°C overnight. This temperature was necessary to dry the samples completely by being above the highest oligomeric T_g of the three materials, but below the lowest T_m of the materials.

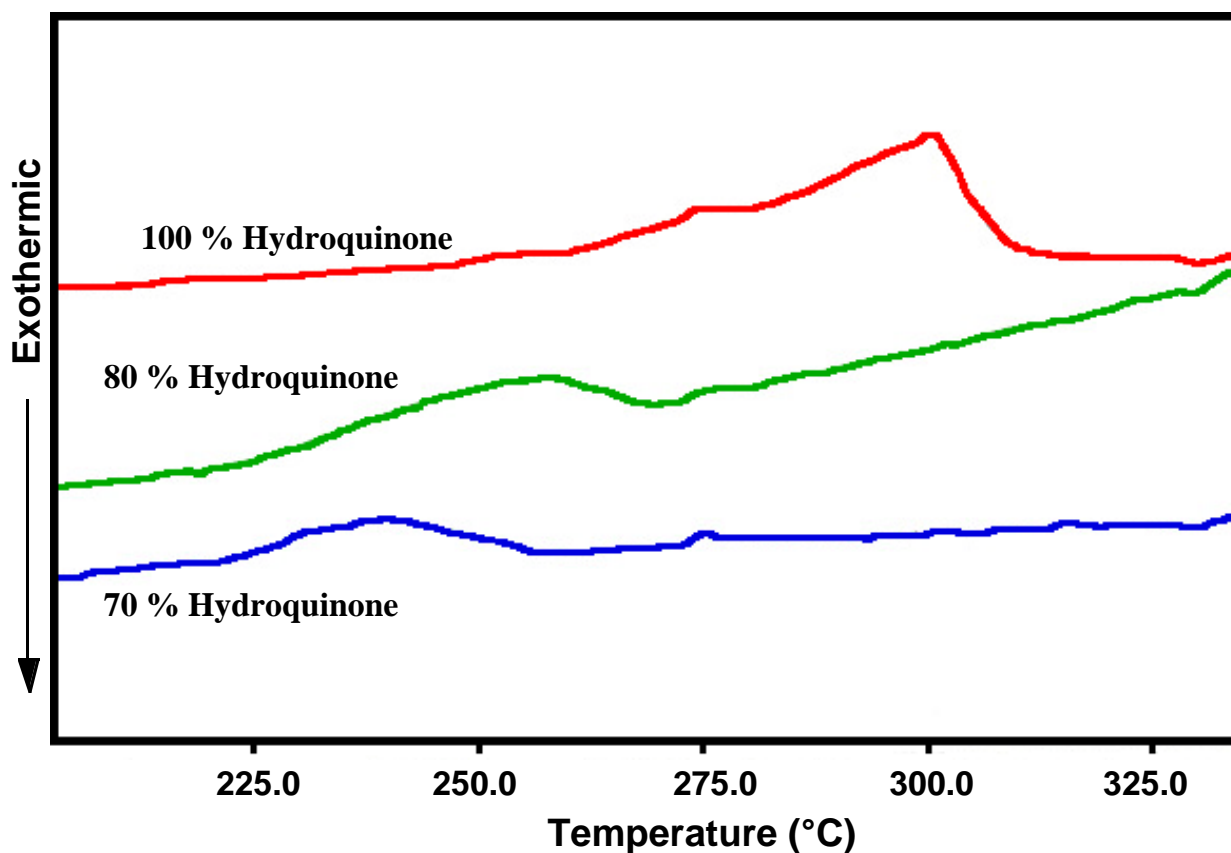


Figure 4.25 DSC Thermograms of Semi-crystalline 5,000 g/mole Phenylethynyl Terminated Poly(arylene ether sulfone) Oligomers from the First Heat at 10°C/min.

Table 4.7 Heats of Fusion of Semi-crystalline 5,000 g/mole Phenylethynyl Terminated Poly(arylene ether sulfone) Oligomers

Oligomer Composition	Heat of Fusion (J/g)
100:0 Hydroquinone:Biphenol	23
80:20 Hydroquinone:Biphenol	18
70:30 Hydroquinone:Biphenol	13

4.5.3 Thermal Transitions of Thermosets

DSC Results

The glass transition temperatures of the materials cured to high gel fractions and measured from the second heat of the DSC are provided in table 4.8. The gel fractions are included for the samples which were cured into molded films. The glass transition temperatures of the high molecular weight thermoplastics are also included as a point of reference. All of the cured T_g s are substantially higher than the oligomer T_g s as expected, and show increases from 30-80°C, depending on the oligomer molecular weight. The reaction mechanism of the network forming reaction is not known,¹²⁰ but it is reasonable to assume that the oligomer molecular weight is correlated with the molecular weight between crosslinks (M_c). As the molecular weight between crosslinks decreases the T_g of the cured material should increase. This trend is observed here except in the case of the 4,4'-biphenol system where there seems to be a slight discrepancy. This discrepancy may be related to the difference in the gel fractions of the 3,000 and 5,000 g/mole cured materials.

The gel fraction is also related to the T_g and low gel fraction indicates that more of the material was not incorporated into the network and could still exist as lower molecular weight soluble chains. A miscible blend of thermoset and low

Table 4.8 Glass Transition Temperatures of Cured Phenylethynyl Poly(arylene ether sulfone)s from the Second Heat of the DSC at 10°C/min.

Bisphenol	Target Mn	T_g¹ (°C)	% Gel
Bisphenol A	thermoplastic control	190*	0
	2,000	205	93
		196²	
	3,000	188	78
	5,000	-	-
Hydroquinone	thermoplastic	217*	
	3,000	212	97
	5,000	208	93
4,4'-Biphenol	thermoplastic	230*	-
	3,000	229	86
	5,000	234³	90
50:50 HQ:BP	5,000	228³	90
60:40 HQ:BP	5,000	222²	-
70:30 HQ:BP	5,000	-	-
80:20 HQ:BP	5,000	214²	-

1-cured in a mold at 370°C for 90 min unless otherwise indicated

2-cured for at 370°C for 2 hours in the DSC under nitrogen

3-cured in a mold at 370°C for 2 hours

*literature value

molecular weight chains should provide a T_g intermediate to those of the two component materials. The presence of a higher sol fraction in the 3,000 g/mole 4,4'-biphenol cured polymer explains the lower T_g relative to the high gel fraction 5,000 g/mole cured polymer network.

The relatively modest increase in cured T_g s to the analogous values of the high molecular weight thermoplastics was somewhat surprising. In other seemingly analogous phenylethynyl imide systems^{134,147} increases in the T_g of the cured system over the thermoplastic system can approach 40-60°C. In this particular system the T_g of the cured polymers was found to be quite similar to the T_g of the thermoplastic materials. One possible explanation for this behavior is that there is a prevalent chain extension reaction taking place during the curing of these oligomers. This could, in principle extend the molecular weight between crosslinks to produce a T_g similar to the high molecular weight linear thermoplastic.

DMA Results

The T_g s from the dynamic mechanical analysis results of four cured films are shown in table 4.9. These data were derived from the same batch of oligomer as the films for the DSC results and nominally under the same conditions. All of the gel fractions were very

Table 4.9 Glass Transition Temperature of Cured Phenylethynyl Poly(arylene ether sulfone)s from DMA at 1°C/min

Bisphenol	Target Mn	T_g (°C)	% Gel
Bisphenol A	5,000	217	91
Hydroquinone	3,000	219	94
4,4'-Biphenol	3,000	229	86
4,4'-Biphenol	5,000	242	91

close, except the 3,000 g/mole 4,4'-biphenol system which was the same film as used in the DSC. The T_g s based on the DMA Tan δ peak are 7-10 °C higher than those by DSC, with the exception of the 3,000 g/mole 4,4'-biphenol which shows no difference in the T_g . It is not unusual for such differences in the T_g s measured by DMA and DSC to be found, especially in thermosets where the DSC transition is weak or very broad. The 3,000 g/mole biphenol cured polymer showed a lower gel fraction than the other materials, and this could be the reason for its behavior.

4.6 Adhesive Properties of Thermosets

One main objective of this research was to design materials suitable for use as aerospace structural adhesives. The method chosen to evaluate the adhesive strength of the materials was the single lap shear test at room temperature. The ASTM D1002 test is a very commonly used test due to its simplicity, even though the mechanics analysis is complex. A pictorial representation of a lap shear bond is presented in figure 4.26. There are drawbacks to this test method, related to the similarity of the bond size and the test forces to actual use conditions, but as a comparative test it can serve its purpose well.¹⁴⁸ The adhesive strengths are provided in table 4.10 for the cured phenylethynyl terminated poly(arylene ether sulfone)s. The tests were carried out on Ti-6Al-4V coupons with presurface treatment. The initial measurements were done using commercially available Pasa-Jel 107 surface treatment.¹⁴⁹ Some of these materials were retested using a chromic acid anodization treatment¹⁴⁹ to compare the two surface treatments. An apparent enhancement of adhesive strength was observed with the latter method and the chromic acid anodized surface treatment was used in the preparation of subsequent samples. Four lap shear samples of each polymer were made concurrently and tested under identical conditions.

All of the samples failed cohesively within the glass fabric/polymer matrix. There is some question as to where within that loci the failure occurs, for

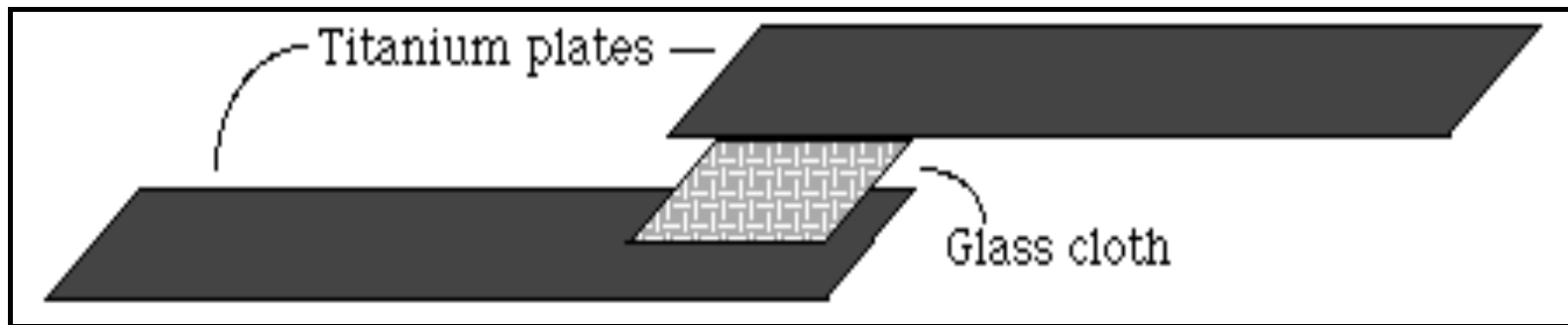


Figure 4.26 Picture of a Single Lap Shear Bond

example it is possible that it is occurring at the interface between the glass cloth and the polymer. The glass cloth serves two purposes. The first is to provide mechanical support for the oligomers which do not have self supporting film properties and the second is to control the bond thickness in the lap shear bond itself. The lap shear results were highly dependent on the bonding conditions: pressure, time and temperature. Pressure was found to be important mainly because of its effect on the bond thickness. A standard pressure of 75 psi was used for all of the bonds so as to obtain comparative numbers. When a higher pressure of 150 psi was used there was a greater amount of material squeezed out during the bonding procedure, reducing the bond thickness and adhesive strength. Time and temperature conditions were chosen to provide bonds with high gel fractions. The same conditions that provided highly cured films were used for the bonding.

The adhesive strengths appear to be good and were comparable to related phenylethynyl polyimide materials,^{14,134,147}. There is a molecular weight dependence evident in each of the systems, e.g., the lower molecular weight oligomers cure to higher glass transition temperatures, but provide lower adhesive strengths. These are related phenomena and are both related to the density of the network formed in the curing reaction. Presumably, the failure of the bond is related to the mechanical strength of the material. It is expected that a

material with a denser network will be less ductile and therefore display a lower adhesive strength.

The effect of the surface treatments on the adhesive strengths is evident and the chromic acid anodized treatment gave improved values relative to the Pasa-Jel treatment. All of the samples failed cohesively so it is not immediately obvious why there is a difference in the results. One may speculate that perhaps the initial failure starts at the interface, but quickly migrates into the bulk adhesive. This would explain the improvement of adhesive strength by different surface treatments in the case of uniform cohesive failure, however, there is no additional evidence to dispute or support that theory.

Table 4.10 Single Lap Shear Results for Cured Phenylethynyl Poly(arylene ether sulfone)s

Bisphenol	Target Mn (g/mole)	Adh.Strength* Pasa Jell (psi)	Adh. Strength* CAA (psi)
Bisphenol A	2,000	3060** ± 200	
Bisphenol A	3,000	3410** ± 100	
Bisphenol A	5,000	3850** ± 470	
Hydroquinone	3,000	3080** ± 250	
Hydroquinone	5,000	3590** ± 180	4450*** ± 510
Biphenol	3,000	2060*** ± 240	2760*** ± 350
Biphenol	5,000	2720*** ± 450	4090*** ± 250
60%HQ:40%BP	5,000		3720*** ± 200
70%HQ:30%BP	5,000		4050*** ± 160

*avg. of 4 samples

**curing conditions: 75psi/370°C/90 min

***curing conditions: 75psi/370°C/120 min

4.7 Mechanical Properties of Composite Panel

Another objective for the development of these materials is their use as carbon fiber composite matrices for aerospace applications. In the case of the adhesives a high adhesive strength was the highest priority and it appears that higher molecular weight oligomers are the best choices for this type of application; it may even be better to use even higher molecular weight oligomers. Although increasing the oligomer molecular weight should increase the adhesive strength to a point, it is also critical to have high solvent resistance and sufficient T_g . Both would be compromised to an extent as the molecular weight of the oligomer is increased. Melt processability and a high T_g are important variables for the aerospace composite matrix application. In the carbon fiber reinforced composite, the fibers largely provide the stiffness and mechanical strength necessary to the application, so a somewhat less tough matrix may be tolerated for some applications. Processability is an important factor in obtaining a good quality composite, since it is necessary to obtain good wetting of the fibers and low voids formation in the final panel/structure. Lower molecular weight oligomers which should provide better flow properties and a higher cured T_g , which lead to better temperature stability and solvent resistance.

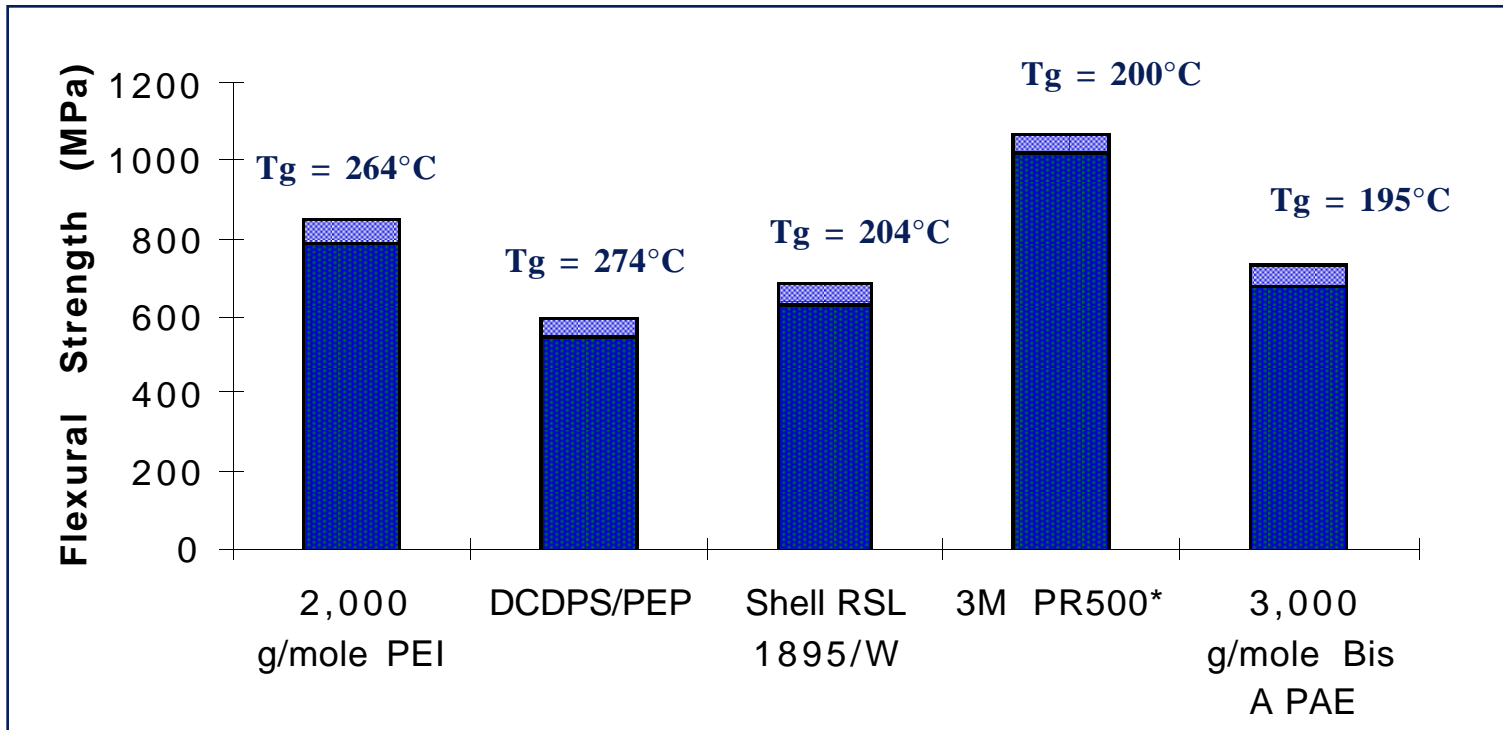
A composite panel was made by resin infusion molding using a 3,000 g/mole bisphenol A based phenylethynyl terminated poly(arylene ether sulfone)

and AS4 woven carbon fiber fabric to demonstrate processibility. The flexural strength mechanical properties were measured for this panel. The fabrication was performed by adding powder into the mold and consolidating the system at 370°C, using a heating rate in the press of 3°C/min. This heating rate allowed the material to flow well above T_g before the cure began to take place, and the processing window encouraged penetration and wetting of the carbon fibers. The low viscosity of the material during processing produced a large amount of flash, which increased the fiber volume fraction from the desired 60% to around 68%. The resulting 6" x 6" panel showed no large voids by C-scan, but the presence or absence of small voids was difficult to ascertain because a AS4-PW-3k fabric was used to fabricate the panel and the ultrasonic C-scan was unable to obtain good resolution through this type of fabric. There was visual evidence of the presence of some very small voids when the panel was cut open. The C-scan also indicated that there appeared to be a higher volume fraction of fiber at one end of the panel than at the other. Obviously, this manufacturing process would need considerable optimization to obtain panels with optimal properties.

Flexural testing was carried out on this panel and flexural strength values are provided in figure 4.27. They were compared to two other materials which were synthesized and manufactured at Virginia Tech and to two commercial epoxy systems. The average value is reported for 5 sample bars from one panel

and the positive standard deviation is indicated on each bar. The first bar is a phenylethynyl terminated polyimide and the second is a very low molecular weight phenylethynyl terminated ether sulfone resin. The third and fourth bars are commercial epoxy systems and the last bar is the previously mentioned poly(arylene ether) of this study. The flexural strength values are comparable, however none of the VT systems have been optimized as only one panel was made of each. Mechanical properties of subsequent panels could likely improve with improved manufacturing technique. The epoxy systems are only being used as a convenient reference in this case. The thermal stability of the epoxy systems is much lower than any of the VT systems and would not be appropriate for use in many high performance aerospace applications.

The warp flexural test was conducted on three panels made under essentially the same conditions although with slightly different consolidation temperatures and times depending on the resin. The consolidation time and temperatures used corresponded to the curing conditions necessary to achieve a high gel fraction in the cured material. The 3,000 g/mole bisphenol A based polysulfone was compared to a low molecular weight phenylethynyl terminated sulfone resin and a 2,000 g/mole phenylethynyl terminated Ultem® based polyimide. The results in table 4.11 indicate some of the relative mechanical properties of these three phenylethynyl based thermoset composites. The flexural



* 3-point bend, whereas, all others were 4-point bend

- average of 5 specimens

Figure 4.27- Comparative Flexural strength of AS4-PW-3k composite panels with a Variety of Thermosetting Resins

strength is essentially a measure of the flexural deformation of the panel. The flexural modulus is a measure of the overall strength of the material to ultimate failure. Thus, the results of these tests indicate that the low molecular weight resin is quite brittle. This makes sense structurally because the concentration of phenylethynyl groups is highest in this material and it should have the highest crosslink density and lowest molecular weight between crosslinks, which is consistent with the high T_g of this material. This material also shows the highest flexural modulus which is also indicative of a highly crosslinked material. The bisphenol A based oligomer has a higher uncured molecular weight than the polyimide, however the backbone structures are completely different so the difference in strength and modulus

Table 4.11 Warp Flexural Test (ASTM D 790-92) Results on AS4-3k-PW Carbon Fabric Composite Panels

Matrix Material	Flex. Strength (MPa)	Flex. Modulus (GPa)	T_g (°C)
3,000 g/mole Bis A Polysulfone	678 ± 55.9	84.8 ± 0.6	195
2,000 g/mole PE-Ultem Polyimide	790 ± 66	73.8 ± 1.9	264
PE-Sulfone Resin	549 ± 54.3	101 ± 15.6	274

could be due to that. The polysulfone has a lower strength and a higher modulus value. These two facts correlate well with the observed results.

The results from the manufacture and testing of this composite panel were considered promising. Optimizing the materials and conditions for these composites should be done in the future. It appears that the properties of the composites will be good and the processing conditions not too rigorous for these low molecular weight materials which have good flow characteristics. One reason why it is important to develop the composite matrices along with the structural adhesives is that the adhesives will not only be used to bond Ti to Ti but also to bond Ti to composites. If the composite is of the same structure as the adhesive the adhesion should be better and may require little or no surface pre-treatment.

4.8 Oligomers Terminated with Different Phenylethynyl

Endcappers

The phenylethynyl compounds described earlier were used to control the endgroups of a 5,000 g/mole bisphenol A based poly(arylene ether sulfone). This afforded a series of phenylethynyl terminated oligomers wherein the electronic environment of the connecting group between the phenylethynyl moiety and the polymer backbone was systematically changed from highly electron withdrawing, phenylethynylphthalimidophenol (PEPIP), to electron donating, 3-phenylethynylphenol (3-PEP). Two of the endcappers, 4-fluoro-4'-phenylethynyldiphenylsulfone (PEFDPS) and 4-fluoro-4'-phenylethynylbenzophenone (FPEB), were added to the polymerization reaction as monofunctional activated halides. 3-PEP was added to the polymerization reaction as a monofunctional phenol and the fourth oligomer was based on the reaction of PEPIP as a monofunctional phenol. The fourth oligomer was actually prepared by first synthesizing a amine terminated oligomer using 3-aminophenol as a monofunctional phenol endcapper and then reacting the amine endgroups with phenylethynylphthalic anhydride. The synthesis of the oligomer directly using PEPIP was unsuccessful because the imide linkage in the endcapper was quickly hydrolyzed by the potassium carbonate and water present during the nucleophilic aromatic substitution polymerization. It should be noted that the

polymer formed in this manner does not have the exact same structural features as are present in the endcapper alone because the endcapper was made using 4-aminophenol. This may have some small affect on the electron withdrawing nature of the imide carbonyls which are para and meta to the ethynyl group.

4.8.1 Characterization of the 5,000 g/mole Phenylethynyl Terminated Oligomers

The endgroup control with the electron withdrawing endcappers may not be as optimal as in the case of the 3-phenylethynylphenol. Table 4.12 shows the molecular weights as calculated from NMR and GPC results along with the % discrepancy in the results. Almost all of the polymers made using 3-phenylethynylphenol showed discrepancies in the 0-10% range. The 5,000 g/mole 3-PEP oligomer show the highest % discrepancy of all of the PEP polymers synthesized.

The reason for the greater error in these polymers molecular weights has not been determined. One obvious reason would be material purity; however the materials seemed to be quite pure by all the characterization methods used. Very small impurity problems should have been overcome in the case of both the PEFDPS and the FPEB because the endcapper was added at the end of the reaction, in slight excess. Possibly, the reaction should have been continued

Table 4.12 Molecular Weight Results for 5,000 g/mole Bisphenol A Based Oligomers Endcapped with a Series of Phenylethynyl Endcappers

Endcapper	^{13}C NMR M_n (g/mole)	GPC M_n (g/mole)	Discrepancy (%)
3-PEP	5500 \pm 350	4500	18
FPEB	6250 \pm 150	4000	36
PEFDPS	6500 \pm 650	4550	30
PEPIP	9100 \pm 1850	5700	37

longer after addition of the endcappers to ensure complete incorporation of the endcappers. Regardless of the reason, the incorporation of endgroups is sufficiently similar for these polymers to be used in a FTIR kinetic study to elucidate any differences in the rate of the disappearance of the phenylethynyl moiety. More characterization of these polymers should be done. Initial results of the curing of the FPEB and PEFDPS terminated oligomers indicate that gel fractions of 96% can be obtained under standard curing conditions of 370°C for 120 minutes. This evidence suggests that these oligomers are in fact fully functionalized and that the origin of the molecular weight discrepancy lies in either the NMR or the GPC data in these cases.

It was mentioned in section 4.2.5 that the shifts in the ethynyl carbons of the endcappers were related to the electronic environment affecting them. The ethynyl regions of the ^{13}C NMR spectra are provided for the polymers in figure 4.28. The tabulated values for the shifts of these peaks are provided in table 4.13. The difference in the shifts of the two ethynyl carbons is different for the polymers than for the unreacted monomers with the comparative effects of the electron withdrawing groups being less in the polymers. A pronounced trend is still visible in the NMR spectra of the polymers which indicates that there really is an electronic difference in the ethynyl carbons of the polymers which may be used to interpret reaction kinetics for the different systems.

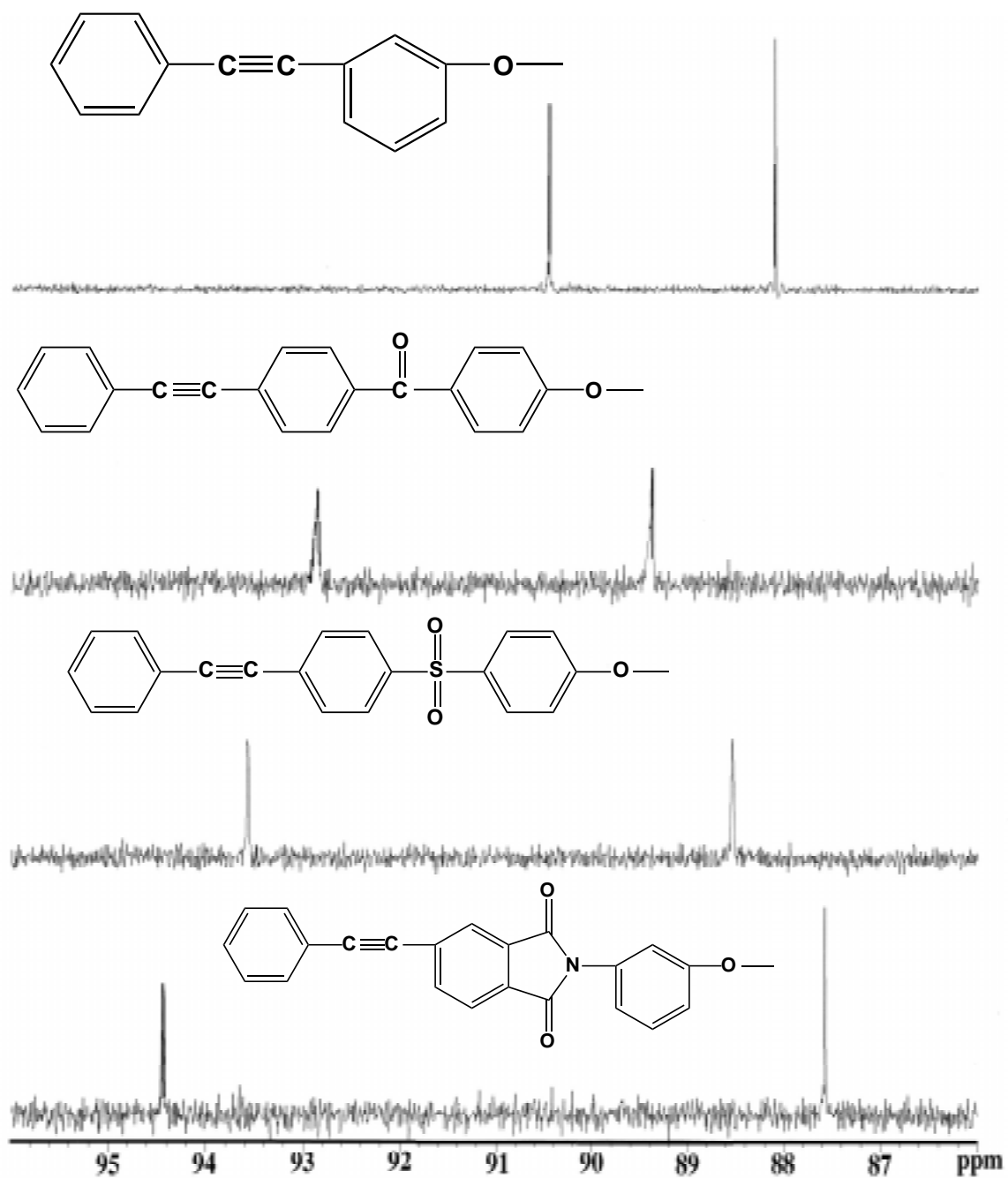


Figure 4.28 Ethynyl Carbon Shifts in ^{13}C NMR of Phenylethynyl Terminated Bisphenol A Based Oligomers

Table 4.13 ^{13}C NMR Shifts of Ethynyl Carbons in Phenylethynyl Terminated Bisphenol A Based Poly(arylene ether sulfone)s

Endcapper	Cα shift (ppm)	Cβ shift (ppm)	Cβ-Cα
3-PEP	88.1	90.4	2.3
FPEB	89.4	92.8	3.4
PEFDPS	88.5	93.6	5.1
PEPIP	87.6	94.4	6.8

The thermal and gel fraction data are reported in table 4.14 for the series of bisphenol A oligomers and their corresponding thermosets. The glass transition temperatures for the uncured oligomers vary a little with the endgroup. They are all in the same molecular weight range, about 5,000 g/mole, and have the same polymer backbone. In this molecular weight range, small differences in the molecular weight can greatly influence T_g . The ^{13}C NMR data provided molecular weights which would fit well with the T_g data obtained from the DSC. The molecular weight calculated for the 3-phenylethynylphenol oligomer was about 1,000 g/mole less than the other two oligomers and the T_g is correspondingly about 10°C less than the other two. The T_g data does not agree well with the molecular weights obtained by GPC.

The oligomers were all cured in the DSC using a cure cycle of 370°C for 2 hours and the T_g was then obtained from a dynamic temperature scan. The T_g s of the thermosets increase with relative electron withdrawing ability of the functional group in the meta/para position relative to the phenylethynyl group. A higher T_g is consistent with a more highly crosslinked network. The polymer backbone is the same so the only difference must be in the network linkages. The T_g data indicates that as the functionality linking the phenylethynyl group to the backbone changes from meta (inductive) electron donating to para (resonance) electron withdrawing the network becomes more dense. This is interpreted as

Table 4.14 Thermal and Cure Characteristics of Bisphenol A Based Oligomers Terminated with Different Phenylethynyl Endcappers

Bisphenol	Endcapper	Oligomer T_g^1 (°C)	Thermoset T_g^2 (°C)	Gel Fraction³ (% gel)
Bisphenol A	PEP	153	198	91
	FPEB	166	206	97
	PEFDPS	162	215	97

1-second heat in the DSC at 10°C/min

2-second heat in the DSC after cure at 370°C/120 min in N₂

3-extracted with Chloroform for 4 days

being due to an increased ratio of crosslink to chain extension. The crosslink site requires three (or more) chains to react together whereas a chain extension site requires only two chains to have reacted.

The gel fractions of the thermosets were obtained from films which were cured under nitrogen in an oven for 120 minutes at 370°C. Higher gel fractions in the crosslinked networks indicate that 3-phenylethynylphenol oligomer was less reactive than the other systems. Apparently it is more difficult for the 3-phenylethynylphenol oligomers to converge to react at the same site. The T_g of the high molecular weight bisphenol A based polysulfone is 190°C while the T_g of the crosslinked network should be higher. A miscible blend of the network and oligomer or high molecular weight branched polymer would provide a lower T_g than a material which consisted of only the crosslinked network. Since the sol fraction was greater for the 3-phenylethynylphenol thermoset, the fact that the T_g is lower than for the carbonyl and sulfone based thermosets may be rationalized.

The single lap shear adhesion results are presented in table 4.15 for the phenylethynyl terminated bisphenol A based thermosets. The 3-phenylethynylphenol thermoset was prepared using a pasa jel surface treatment which has been shown to provide consistently lower adhesion strengths than the chromic acid anodized surface treated samples. This may be one reason why the difference in the adhesion strengths of these materials is so pronounced. The difference is present in the carbonyl and sulfone based materials as well though not to a great extent. These values are much higher than other arylene ether phenylethynyl endcapped oligomers. These values are in the range of 5,000 psi (35 MPa) which compares very well with phenylethynyl terminated imide

materials^{14,134,147}. This indicates that higher crosslink density could have a large effect on the adhesion strength of this type of material to titanium.

Table 4.15 Single Lap Shear Results for Cured Bisphenol A Based Oligomers with Different Phenylethynyl Endcappers

Bisphenol	Endcapper	Adhesive Strength* (psi)
Bisphenol A	PEP	3850 ± 470**
	FPEB	4680 ± 260
	PEFDPS	4890 ± 520

* average of 4 samples, cured at 370°C/120 min., chromic acid anodized

** avg. of 4 samples, cured at 370°C/90 min., pasa jel treatment

4.8.2 Kinetic Study of the Cure of Phenylethynyl

Terminated Poly(arylene ether sulfone)s by FTIR

The curing mechanism of the phenylethynyl moiety in oligomers is unknown and is in need of further investigation. There is an apparent difference in the curing behavior of the ether linked phenylethynyl groups on a 3-phenylethynylphenol terminated poly(arylene ether sulfone) and a polyimide terminated with 4-phenylethynylphthalic anhydride, as evidenced by curing times and thermoset T_g s. The polyimide can be cured in a faster time, 60 min. vs. 120 min, to a higher gel fraction and a higher increase in the glass transition temperature is achieved, which corresponds to a greater degree of crosslinking. These differences can not be attributed to the backbone molecular structure and the phenylethynyl endgroups are identical. The only difference in the materials other than the backbone is the linking structure which connects the endgroup to the backbone. In the case of the phenylethynylphenol the endgroup is meta to a electron donating ether. In the case of the phenylethynylphthalic anhydride the endgroup is para and meta to electron withdrawing carbonyls.

There is some evidence to indicate that an electron withdrawing group in a position to resonance stabilize a radical can increase the rate of the curing reaction.¹²⁴ The theory assumes the reaction does take place via a free radical

mechanism and by stabilizing the radical formed in the initiation step the reaction may proceed with a lower activation energy and therefore, cure faster.

The kinetic study of the curing reaction of the four phenylethynyl capped 5,000 g/mole bisphenol A based polymers was designed to investigate the effect of the electron withdrawing capacity of the linking structure on the rate of cure and activation energy of the cure reaction. In each compound there is an electron withdrawing group in the para position to the ethynyl carbons except for 3-phenylethynylphenol. FTIR experiments were attempted to monitor the cure of the four phenylethynyl terminated oligomers with varying electronic structure. The materials were cured at two different temperatures, 320°C and 350°C. The disappearance of the ethynyl stretch at around 2200 cm⁻¹ was measured as a function of time and temperature for each compound. Each spectrum was normalized based on the initial spectrum of the series at each temperature. The area of the ethynyl peak was measured with time and the data was treated as a first order reaction. It is clear that over the extent of the curing reaction the data does not fit the model linearly, but certain trends can be observed.

Figure 4.29 shows the disappearance of the ethynyl peak for the sulfone based endcapped (PEFDPS) oligomer at 350°C during the first 15 minutes of the reaction. After 15 minutes, the change in the area of the peak very small.

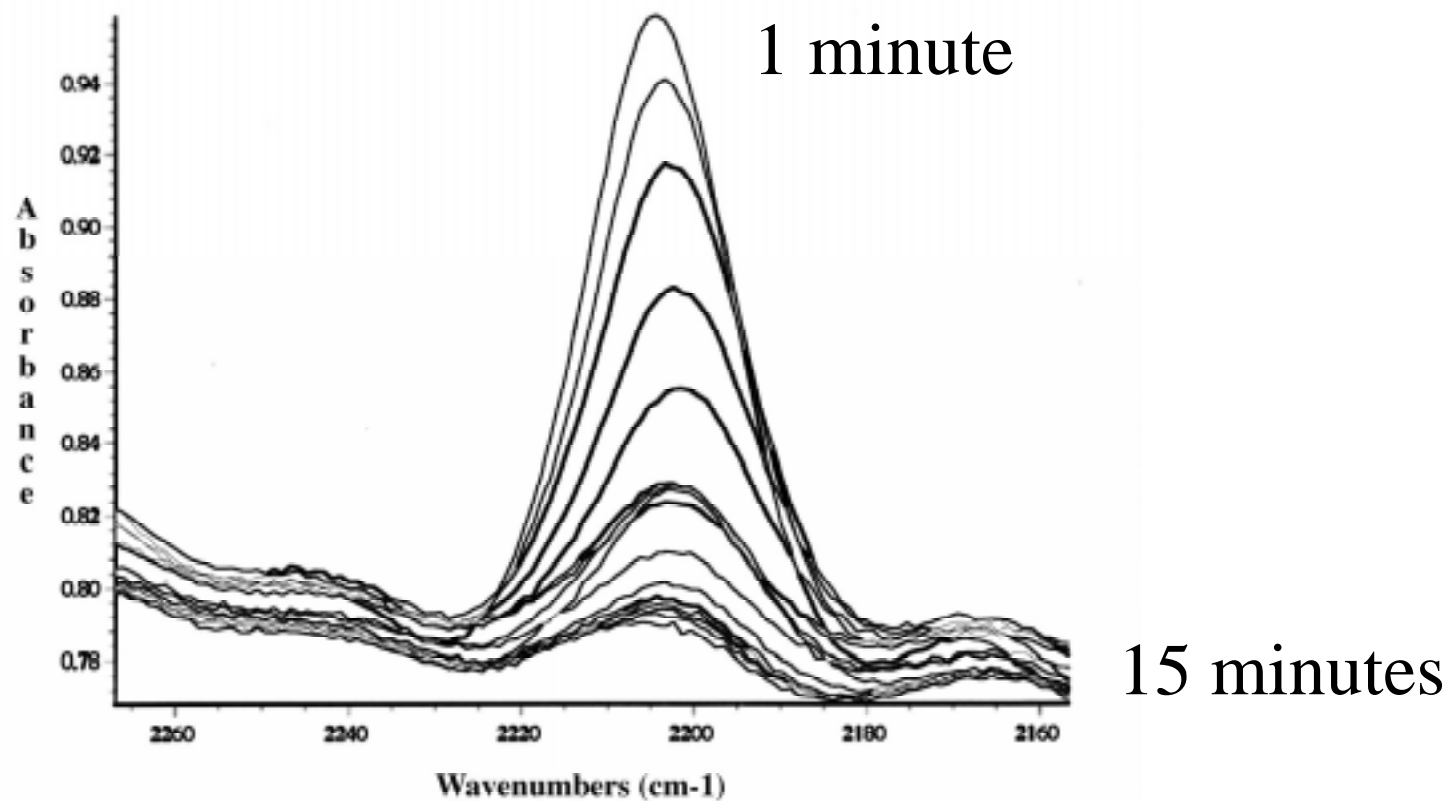


Figure 4.29 FTIR Spectra of a 5,000 g/mole Bisphenol A Based Phenylethynyl Terminated Oligomer Endcapped with a Sulfone Based Endcapper (PEFDPS) Taken Every 1 minute at 350°C.

The data was plotted for a first order disappearance by calculating the natural log of the original peak area divided by the area at each time.¹⁵⁰ Figure 4.30 shows the first order disappearance of the ethynyl stretch in the PEFDPS terminated polymer at 320°C and figure 4.31 represents the same reaction at 350°C. As the peak area became smaller over time the curve leveled off. One thing is clear, the concentration of the ethynyl endgroups reaches a undetectable low level by this infrared method well before the curing reaction is actually complete. Exactly when the complete disappearance of ethynyl groups occurs was not defined.

The FTIR spectra illustrating the disappearance of the ethynyl group at 350°C for a 5,000 g/mole bisphenol A based phenylethynyl polymer terminated with the carbonyl containing endcapper, FPEB, are shown in figure 4.32. The peak due to the ethynyl stretch is very small initially in the reaction, rendering the measurement very difficult as the peak area quickly reached undetectable levels. The first order disappearance of this peak at 350°C is shown in figure 4.33. The very small size of the peak produces a great deal of scatter in the data.

The ethynyl peaks were very small due not only to concentration effects but because of the inherently symmetrically substituted ethynyl stretches are known to be of low magnitude. The ethynyl peaks in the oligomers with the electron withdrawing

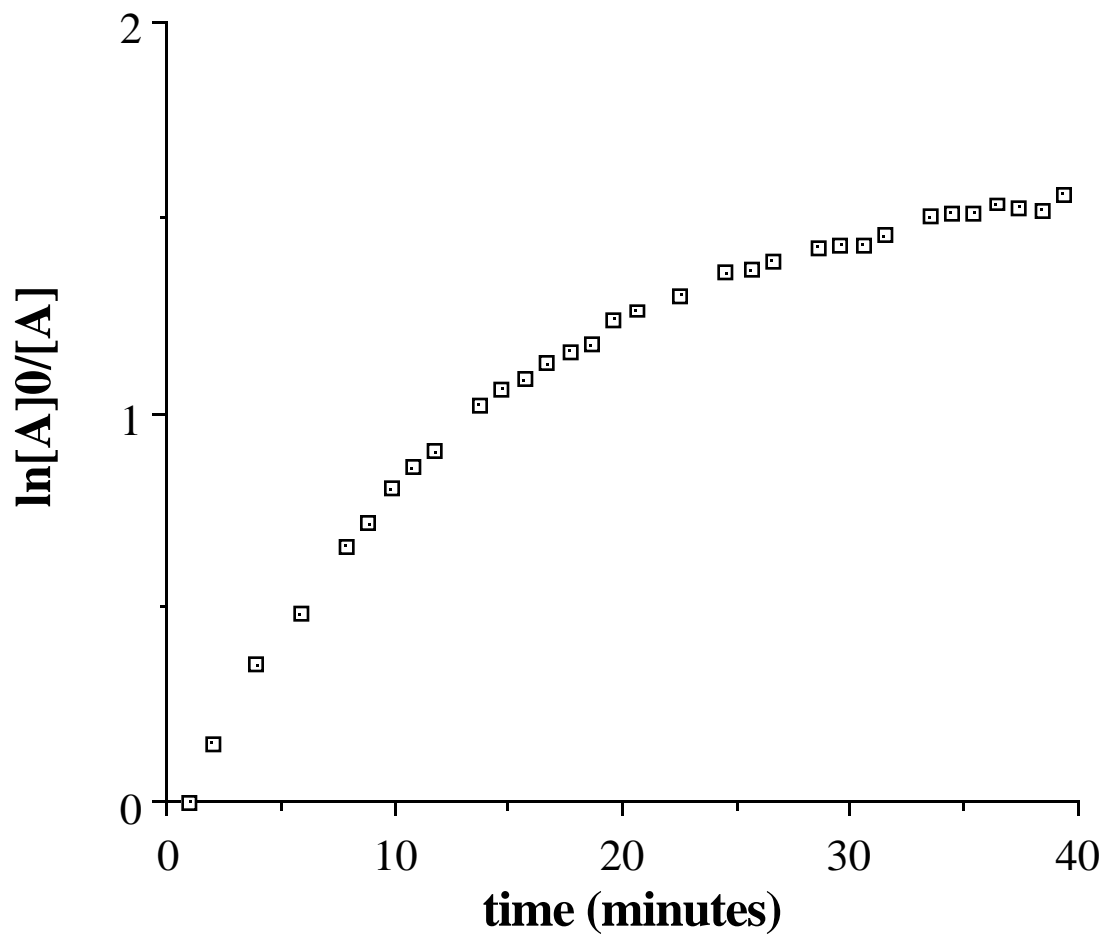


Figure 4.30 Disappearance of the Ethynyl Stretch with Time in a PEFDPS Terminated Poly(arylene ether sulfone) at 320°C Assuming First Order Kinetics

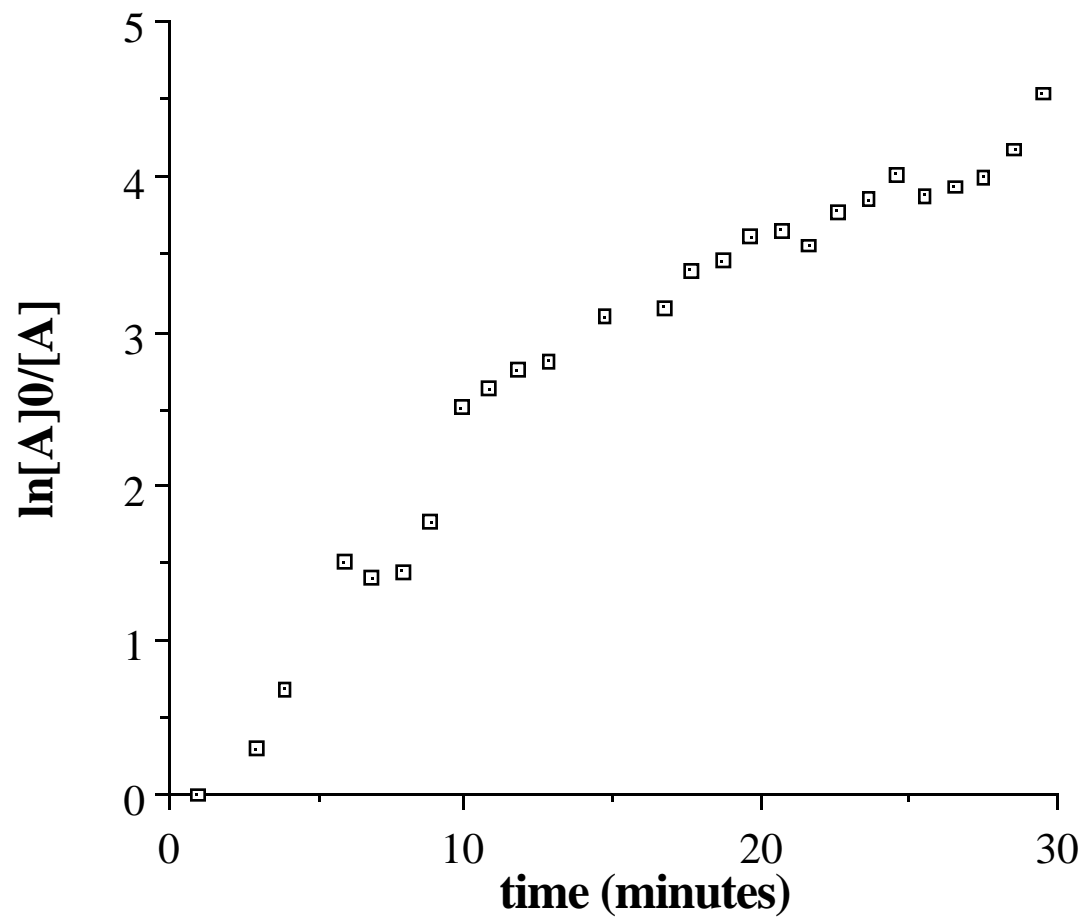


Figure 4.31 Disappearance of the Ethynyl Stretch with Time in a PEFDPS Terminated Poly(arylene ether sulfone) at 350°C Assuming First Order Kinetics

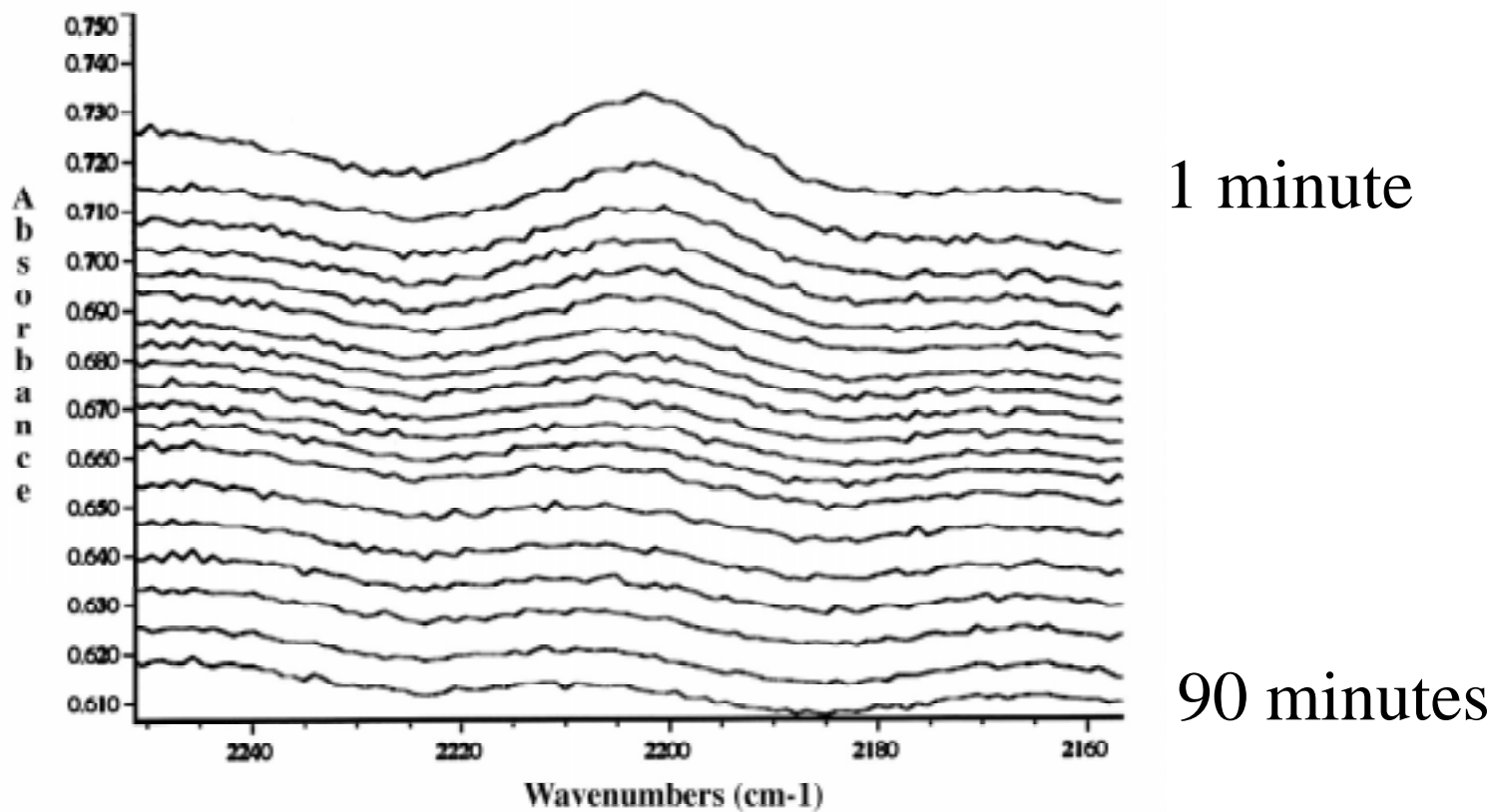


Figure 4.32 FTIR Spectra of a 5,000 g/mole Bisphenol A Based Phenylethynyl Terminated Oligomer Endcapped with a Carbonyl Based Endcapper (FPEB) Taken Every 5 minutes at 350°C.

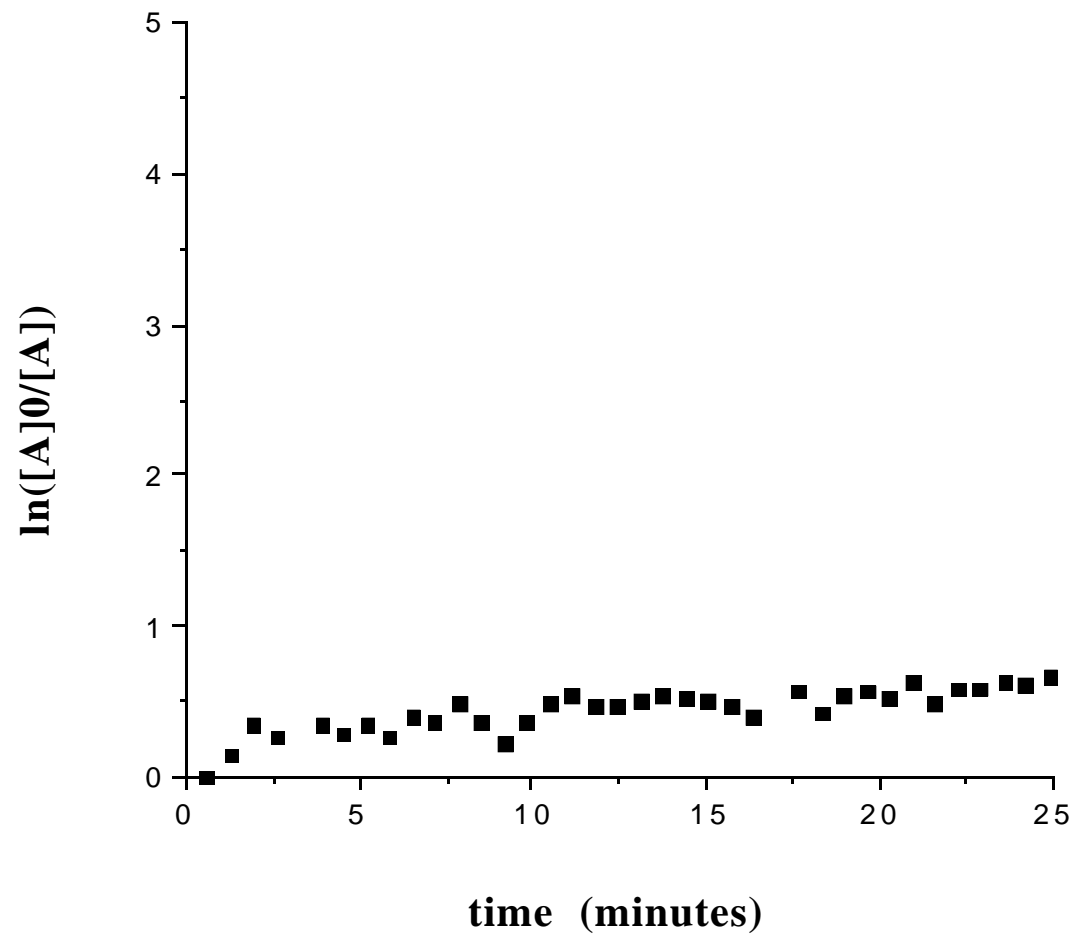


Figure 4.33 Disappearance of the Ethynyl Stretch with Time in a FPEB Terminated Poly(arylene ether sulfone) at 350°C Assuming First Order Kinetics

groups had larger ethynyl peaks than the 3-phenylethynylphenol based material and in the materials with a larger the electron withdrawing effect on the ethynyl carbons the ethynyl stretch was observed to be larger initially. This same electron withdrawing effect was also observed by ^{13}C NMR where there was a difference in the shifts of the two ethynyl carbons related to the effect of the electron withdrawing substituent.

It is possible to say that the reactions proceed at much greater rates as the temperature is increased from 320 to 350°C. The initial disappearance of the ethynyl group is basically linear and by assuming first order behavior in this region, calculation of apparent rate constants for each compound and temperature can be achieved. The smaller ethynyl peaks provided much more scatter in the data which led to a much poorer fit to the line. The initial rate constants are provided in table 4.16. These rate constants were calculated for the first 15 minutes of the reaction in all cases. This time corresponded to different levels of conversion depending on the material and the temperature. The rate constants calculated for the PEFDPS system had correlation coefficients of about 0.98 while the correlation coefficient for the FPEB system was much lower, 0.71, due to a large amount of scatter in the data believed to be related to the small area of the peak. The relative differences in the slope of the disappearance are visible even if the

Table 4.16 **Apparent First Order Rate Constants for Phenylethynyl Terminated Oligomers Cured in the FTIR**

Endcapper	k at 320°C (s⁻¹)	k at 350°C (s⁻¹)
PEFDPS	0.076	0.254
FPEB	-	0.016

reaction can not be said to be strictly first order. It seems clear that the disappearance of the ethynyl group in the carbonyl containing compound takes place at a much reduced rate from the sulfone containing compound and that the disappearance occurs at a slower rate at lower temperatures.

Chapter 5 Conclusions

A systematic series of phenylethynyl terminated poly(arylene ether sulfone) oligomers based on either bisphenol A, hydroquinone or biphenol based homo- or copolymer systems have been synthesized and characterized. Curing of the phenylethynyl group was successfully conducted to prepare network thermoset materials from the precursor very processible oligomers. The properties of the thermosets were evaluated for their suitability for applications such as aerospace structural adhesives and/or as polymer matrices for polymer/carbon fiber composites.

3-Phenylethynyl phenol has been demonstrated to be useful as an endcapping agent to control both molecular weight and endgroup structure in poly(arylene ether sulfone)s. The phenylethynyl endgroup provides a structure which is capable of a thermal crosslinking reaction at temperatures high enough to provide a substantial processing window for the materials studied.

It has been demonstrated that control of the polymer backbone structure allows for some flexibility in processing and thermal properties. All aromatic homopolymer backbones can provide higher glass transition temperatures but have the drawback of a reduced processing window due to the presence of semi-crystalline regions. Copolymers containing all aromatic backbones can be

tailored to have a much expanded processing window over the homopolymers with only a modest decrease in the T_g of the thermoset.

Initial measurements of the adhesive and composite properties have been completed. These results provide evidence that the thermoset materials show good adhesion to surface treated Ti 6/4. The indications are that mechanical toughness is retained in the crosslinked network that would be expected in the thermoplastic. One composite panel was manufactured to demonstrate feasibility and the results were promising. Processability of the material was good but optimization of the procedure would be required in order to obtain panels with a higher resin content.

New phenylethynyl containing functional compounds have been synthesized and used to endcap poly(arylene ether sulfone) oligomers. In particular, electron withdrawing groups such as sulfone and carbonyl ketone groups were prepared. Investigations into the cure kinetics and mechanical behavior of these thermosets as compared to the 3-phenylethynyl phenol analog were conducted. Initial results indicate that the presence of an electron withdrawing group in the para position of the internal ring of the phenylethynyl endgroup leads to a material with a higher crosslink density, higher T_g , and better adhesion under identical cure conditions.

Chapter 6 References

- (1) R. J. Cotter *Engineering Plastics: A Handbook of Polyarylethers*; Gordon and Breach Publishers:, 1995.
- (2) J. P. Critchley; G. J. Knight; W. W. Wright *Heat-Resistant Polymers: Technologically Useful Materials*; Plenum Press: New York, 1983.
- (3) D. A. Lewis; J. H. O'Donnel; J. L. Hedrick; T. C. Ward; J. E. McGrath *Radiation-Resistant, Amorphous, All-Aromatic Poly(arylene ether sulfones): Synthesis, Physical Behavior, and Degradation Characteristics*; Reichmanis, E. and O'Donnell, J. H., Ed.; American Chemical Society: Washington D. C., 1989; Vol. 381, pp 252-261.
- (4) L. M. Robeson; A. G. Farnham; J. E. McGrath *Dynamic Mechanical Characteristics of Polysulfone and Other Polyarylethers*; Meier, D. J., Ed.; Gordon and Breach, 1978; Vol. 4, pp 405-526.
- (5) P. M. Hergenrother, *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1262-1268.
- (6) J. L. Hedrick; D. K. Mohanty; B. C. Johnson; R. Viswanathan; J. A. Hinkley; J. E. McGrath, *Journal of Polymer Science: Polymer Chemistry Edition* **1986**, *23*, 287-300.
- (7) R. Viswanathan; B. C. Johnson; J. E. McGrath, *Polymer* **1984**, *25*, 1827-1836.
- (8) J. E. McGrath; A. G. Farnham; L. M. Robeson, *Polymer Preprints* **1975**, *16*, 476-482.
- (9) R. N. Johnson; A. G. Farnham; R. A. Clendinning; W. F. Hale; C. N. Merriam, *Journal of Polymer Science: Part A-1* **1967**, *5*, 2375-2398.
- (10) L. M. Robeson; A. G. Farnham; J. E. McGrath, *Applied Polymer Symposium* **1975**, *26*, 373-385.

- (11) G. Meyer; B. Tan; J. E. McGrath, *High Per. Poly.* **1994**, 6, 423-435.
- (12) S. J. Mecham; S. Jayaraman; Y. J. Lee; J. B. Mecham; D. J. Riley; T. E. Glass; J. E. McGrath, *Polymer Preprints* **1995**, 36, 789-790.
- (13) S. Jayaraman; R. Srinivasan; J. E. McGrath, *Journal of Polymer Science: Part A: Polymer Chemistry* **1995**, 33, 1551-1563.
- (14) P. M. Hergenrother; R. G. Bryant; B. J. Jensen; S. J. Havens, *Journal of Polymer Science: Part A: Polymer Chemistry* **1994**, 32, 3061-3067.
- (15) S. J. Mecham; V. Vasudevan; S. Liu; M. M. Bobbitt; S. Srinivasan; A. C. Loos; J. E. McGrath, *Polymeric Materials Science and Engineering Preprints* **1996**, 74, 61.
- (16) S. J. Mecham; S. Jayaraman; M. M. Bobbitt; V. Vasudevan; J. E. McGrath, *Adhesion Society Proceedings* **1996**, 33.
- (17) S. J. Mecham; M. M. Bobbitt; M. E. Pallack; V. Vasudevan; J. E. McGrath, *Adhesion Society Proceedings* **1997**, 211.
- (18) M. M. Bobbitt; S. J. Mecham; V. Vasudevan; J. E. McGrath, *Adhesion Society Proceedings* **1996**, 289.
- (19) A. Ayambem; S. Mecham; Y. Sun; J. E. McGrath, *Polymer Preprints* **1997**, 38.
- (20) R. N. Johnson; A. G. Farnham; U.S. 4,175,175; 1979
- (21) S. Maiti; B. K. Mandal, *J. Polym. Mater.* **1992**, 9, 9.
- (22) B. K. Mandal; S. Maiti, *Eur. Polym. J.* **1986**, 22, 447.
- (23) B. E. Jennings; M. E. B. Jones; J. B. Rose, *Journal of Polymer Science, Part C* **1967**, 16, 715.
- (24) A. G. Farnham; L. M. Robeson; J. E. McGrath, *J. Appl. Polym. Sci. Symp.* **1975**, 26, 373.

- (25) S. J. Pak; G. D. Lyle; R. Mercier; J. E. McGrath, *Polymer* **1993**, *34*, 885-895.
- (26) M. Strukelj; M. Pavent; A. S. Hay, *Macromolecules* **1993**, *26*, 1777-1778.
- (27) M. Strukelj; M. Paventi; A. S. Hay, *Macromol. Symp.* **1994**, *77*, 379-388.
- (28) G. Lucotte; L. Cormier; B. Delfort, *Polymer Bulletin* **1990**, *24*, 577-582.
- (29) P. M. Hergenrother, *Journal of Polymer Science: Polymer Chemistry Edition* **1982**, *20*, 3131-3146.
- (30) M. E. A. Cudby; R. G. Feasey; S. Gaskin; M. e. B. Jones; J. B. Rose, *J. Polym. Sci., Part C* **1969**, *22*, 747.
- (31) J. B. Rose, *Polymer* **1974**, *15*, 456.
- (32) J. B. Rose, *Chem. Ind.* **1968**, 461.
- (33) V. J. Leslie; J. B. Rose; G. O. Rudkin; J. Feltzin, *ACS Symp. Ser.* **1974**, *4*, 63.
- (34) R. N. Johnson *Polysulfones*; Bikales, N. M., Ed.; John Wiley and Sons: New York, 1988; Vol. 13, pp 196.
- (35) E. J. Goethals, *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1968**, *2*, 73.
- (36) M. E. A. Cudby; R. G. Feasey; B. E. Jennings; M. E. B. Jones; J. B. Rose, *Polymer* **1965**, *6*, 589.
- (37) T. E. Attwood; A. B. Newton; J. B. Rose, *Br. Polym. J.* **1972**, *4*, 391.

- (38) J. A. Miller *Aromatic Nucleophilic Substitution*; American Elsevier: New York, 1968.
- (39) J. March *Advanced Organic Chemistry*; Third ed.; John Wiley and Sons: New York, 1985.
- (40) J. Meisenheimer, *Liebigs Ann. Chem* **1902**, 323, 205.
- (41) C. A. Fyfe; A. Koll; S. W. H. Damji; C. D. Malkiewich; P. A. Forte, *Can. J. Chem.* **1977**, 55, 1468.
- (42) G. G. Messmer; G. J. Palenik, *Chem. Commun.* **1969**, 470.
- (43) N. Kornblum; L. Cheng; R. C. Kerber; M. M. Kestner; B. N. Newton; H. W. Pinnick; R. G. Smith; P. A. Wade, *J. Org. Chem.* **1976**, 41, 1560.
- (44) J. F. Bunnett; R. E. Zahler, *Chem. Rev.* **1951**, 49, 273-412.
- (45) F. A. Carey; R. J. Sundberg *Advanced Organic Chemistry*; Third ed.; Plenum Press: New York, 1990.
- (46) R. Alexander; E. C. F. Ko; A. J. Parker; T. J. Broxton, *J. Am. Chem. Soc.* **1968**, 90, 5049.
- (47) R. L. Fuchs; L. L. Cole, *J. Am. Chem. Soc.* **1973**, 95, 3194.
- (48) T. F. Magnera; G. Caldwell; J. Sunner; S. Iduta; P. Kebarle, *J. Am. Chem. Soc.* **1984**, 106, 6140.
- (49) J. E. Harris; R. N. Johnson *Polysulfones*; John Wiley and Sons: New York, 1988; Vol. 13, pp 196-211.
- (50) B. Gerd; C. Claus; Ger. 2,749,645;
- (51) I. C. I. Ltd.; Jap. 7,812,991; 1978
- (52) I. C. I. U.S.; Ger. 2,635,101; 1977

- (53) I. C. Taylor; Ger. 2,733,905; 1978
- (54) R. Viswanathan *Synthesis and Characteristics of Polyarylene Ether Sulfones*; Virginia Polytechnic Institute and State University: Blacksburg, 1981.
- (55) R. Viswanathan; J. E. McGrath, *Polymer Preprints* **1979**, 20, 365.
- (56) S. R. Schulze; A. L. Baron, *Advan. Chem. Ser.* **1969**, 91, 692.
- (57) Duane B. Priddy, Jr., *Synthesis and Characterization of Poly(arylene ether)s Containing Phosphorus, Sulfur and Heterocyclic Pendant Moieties*; Virginia Polytechnic Institute and State University: Blacksburg, 1994.
- (58) J. J. Dumias; A. L. Cholli; L. W. Jelinski; J. L. Hedrick; J. E. McGrath, *Macromolecules* **1986**, 19, 1884.
- (59) L. M. Robeson; S. T. Crisafulli, *J. Appl. Polym. Sci.* **1983**, 28, 2925.
- (60) T. E. Attwood; T. King; V. J. Leslie; J. B. Rose, *Polymer* **1977**, 18, 369.
- (61) S.-C. Lin; E. M. Pearce *High Performance Thermosets: Chemistry, Properties, Applications*; Hanser Publishers: Munich, 1994.
- (62) G. W. Meyer; J. L. Heidbrink; J. G. Franchina; R. M. Davis; S. Gardner; V. Vasudevan; T. E. Glass; J. E. McGrath, *Polymer* **1996**, 37, 5077-5088.
- (63) R. G. Bryant; B. J. Jensen; P. M. Hergenrother, *Polymer Preprints* **1992**, 33, 910.
- (64) T. Dyakonov; J. Drbohlav; P. J. Mann; I. J. Goldfarb; W. T. K. Stevenson, *Polymer Degradation and Stability* **1994**, 46, 357-369.
- (65) D. Garcia, *J. Polym. Sci.: Part B: Polym. Phys.* **1987**, 25, 1581-1594.

- (66) I. J. Goldfarb; C. Y.-C. Lee; C. C. Kuo *Kinetics of Acetylene-Terminated Resin Cure and Its Effects on Dynamic Mechanical Properties*; May, C. A., Ed.; American Chemical Series: Washington D. C., 1983; Vol. 227, pp 49-59.
- (67) P. M. Hergenrother, *Journal of Macromolecular Science-Reviews in Macromolecular Chemistry* **1980**, C19, 1-34.
- (68) P. M. Hergenrother, *Polym. Prepr. Am. Chem. Soc. Div. Org. Coat. Plast. Chem.* **1982**, 46, 165-169.
- (69) B. J. Jensen; R. G. Bryant; P. M. Hergenrother; USA 5,268,444; 1993
- (70) S. Jin; A. F. Yee, *Journal of Applied Polymer Science* **1991**, 43, 1865-1874.
- (71) S. Jin; A. F. Yee, *J. of Applied Polymer Sci.* **1991**, 43, 1849-1858.
- (72) C. C. Kuo; C. Y.-C. Lee; I. J. Goldfarb, *ACS Org. Coat. Plast. Prepr.* **1982**, 46, 595-599.
- (73) C. Y.-C. Lee; C. C. Kuo; I. J. Goldfarb *Acetylene-Terminated Resin Cures: Air and Nitrogen Effects*; May, C. A., Ed.; American Chemical Society: Washington D. C., 1983; Vol. 227, pp 61-81.
- (74) C. L. Leung, *ACS Org. Coat. Plast. Prepr.* **1982**, 46, 322.
- (75) R. L. Levy, *Polymer Preprints* **1982**, 23, 181.
- (76) G. Lucotte; L. Cormier; B. Delfort, *Journal of Polymer Science: Part A: Polymer Chemistry* **1991**, 29, 897-903.
- (77) G. D. Lyle; J. S. Senger; D. H. Chen; S. Kilic; S. D. Wu; D. K. Mohanty; J. E. McGrath, *Polymer* **1989**, 30, 978-985.
- (78) C. Maes; J. Devaux; R. Legras; I. W. Parsons; P. T. McGrail, *Journal of Polymer Science: Part A: Polymer Chemistry* **1994**, 32, 3171-3182.

- (79) C. Maes; J. Devaux; R. Legras; P. T. McGrail, *Polymer* **1995**, *36*, 3159-3164.
- (80) K. Mai; H. Zeng, *Journal of Applied Polymer Science* **1993**, *49*, 2105-2114.
- (81) K. Mai; H. Zeng, *Journal of Applied Polymer Science* **1994**, *53*, 1653-1661.
- (82) W. T. K. Stevenson; I. J. Goldfarb, *Journal of Applied Polymer Science* **1991**, *42*, 665-677.
- (83) W. T. K. Stevenson; I. J. Goldfarb; E. J. Soloski; M. J. Houtz, *Journal of Applied Polymer Science* **1991**, *42*, 679-691.
- (84) V. Vasudevan; S. J. Mecham; S. Liu; S. Srinivasan; S. Claus; A. C. Loos; J. E. McGrath, *SAMPE Proceedings* **1996**.
- (85) J. S. Wallace; F. E. Arnold; W. A. Feld *Synthesis of Bisphenol-Based Acetylene Terminated Thermosetting Resins*; Spinelli, F. W. H. a. H. J., Ed.; American Chemical Society: Washington D. C., 1985; Vol. 282, pp 17.
- (86) P. M. Hergenrother, *Trends in Polymer Science* **1996**, *4*, 104.
- (87) F. L. Hedberg; F. E. Arnold; U. S. 3,876,614; 1975
- (88) F. L. Hedberg; F. E. Arnold, *J. Polym. Sci., Polym. Chem. Ed* **1976**, *14*, 2607.
- (89) F. L. Hedberg; F. E. Arnold, *J. Appl. Polym. Sci.* **1979**, *24*, 763.
- (90) J. J. Harrison; E. T. Selwitz; C. M. Feld; W. A. Unroe; F. L. Hedberg, *Polym. Prepr.* **1982**, *23*, 189.
- (91) P. M. Hergenrother, *Macromolecules* **1981**, *14*, 898.
- (92) P. M. Hergenrother; U.S. 4,375,536; 1983

- (93) P. M. Hergenrother, *Polym. Prepr.* **1981**, 22, 102.
- (94) P. M. Hergenrother, *28th I.U.P.A.C., Macromol. Symp.; Int. Union Pure Appl. Chem.* **1982**.
- (95) P. M. Hergenrother, *J. Appl. Polym. Sci* **1983**, 28, 355.
- (96) P. M. Lindley; B. A. Reinhardt; F. E. Arnold; U. S. 4,731,442; 1988
- (97) P. M. Lindley; B. A. Reinhardt; F. E. Arnold, *Polym. Prepr.* **1987**, 28, 67.
- (98) V. Sankaran; S. C. Lin; C. S. Marvel, *J. Polym. Sci., Polym. chem. Ed.* **1980**, 18, 495.
- (99) R. C. Evers; G. J. Moore; T. J. Abraham, *J. Polym. Sci., Part A: Polym. Chem.* **1988**, 26, 3213.
- (100) R. C. Evers; G. J. Moore; U. S. 4,663,425; 1987
- (101) R. C. Evers; G. J. Moore, *Polym. Prepr.* **1985**, 26, 140.
- (102) J. G. Smith Jr.; J. W. Connell; P. M. Hergenrother, *Polymer Preprints* **1993**, 34, 431-432.
- (103) B. A. Reinhardt; F. E. Arnold; M. R. Unroe; U. S. 4,513,131; 1985
- (104) B. J. Jensen; R. G. Bryant, *Polym. Prepr.* **1994**, 35, 513.
- (105) S. Jayaraman; G. Meyer; T. M. Moy; R. Srinivasan; J. E. McGrath, *Polymer Preprints* **1993**, 34, 513.
- (106) S. Jayaraman; R. Srinivasan; J. E. McGrath, *Polymer Preprints* **1993**, 34, 511.
- (107) W. D. Joseph; J. C. Abed; T. H. Yoon; J. E. McGrath, *Polymer Preprints* **1994**, 35, 551.

- (108) F. W. Harris; A. Pamidimukkala; R. Gupta; S. Das; T. Wu; G. J. Mock, *Macromol. Sci.-Chem.* **1984**, A21, 1117.
- (109) G. W. Meyer; S. Jayaraman; Y. J. Lee; G. D. Lyle; T. E. Glass; J. E. McGrath, *Mater. Res. Soc. Symp. Proc.* **1993**, 305, 3.
- (110) G. W. Meyer; T. E. Glass; H. J. Grubbs; J. E. McGrath, *Journal of Polymer Science: Part A: Polymer Chemistry* **1995**, 33, 2141-2149.
- (111) G. W. Meyer; B. Tan; J. E. McGrath, *High Perform. Polym.* **1995**, 6, 423.
- (112) J. A. Johnston; F. M. Li; F. W. Harris; T. Takekoshi, *Polymer* **1994**, 35, 4865-4873.
- (113) B. J. Jensen; P. M. Hergenrother; G. Nwokogu, *Polymer* **1993**, 34, 630.
- (114) P. M. Hergenrother; J. G. S. Jr, *Polymer* **1994**, 35, 4857-4864.
- (115) S. J. Havens; R. G. Bryant; B. J. Jensen; P. M. Hergenrother, *Polymer Preprints* **1994**, 35, 553.
- (116) F. E. Arnold; U. S. 4,038,320; 1977
- (117) R. G. Bryant; B. J. Jensen; P. M. Hergenrother, *Polym. Prepr.* **1993**, 34, 566.
- (118) J. A. Hinkley, *Journal of Advanced Materials* **1996**, 55-59.
- (119) H. D. Stenzenberger *Addition Polyimides*; Hergenrother, P. M., Ed.; Springer-Verlag: Berlin, 1994; Vol. 117, pp 167-220.
- (120) T. V. Holland; T. E. Glass; J. E. McGrath, *Polymer Preprints* **1997**, 38.
- (121) L.-S. Tan, *Journal of Polymer Science: Part A: Polymer Chemistry* **1987**, 25, 3159.

- (122) K. H. Wood; R. A. Orwoll; B. J. Jensen; P. R. Young; H. M. McNair, *Polymer Prepr.* **1997**, *38*, 266.
- (123) T. Takekoshi; J. M. Terry, *Polymer* **1994**, *35*, 4874-4880.
- (124) S. B. Sastri; T. M. Keller; K. M. Jones; J. P. Armistead, *Macromolecules* **1993**, *26*, 6171.
- (125) R. G. Bryant; P. M. Hergenrother, *High Perform. Polym.* **1995**, *7*, 125.
- (126) S. Gandon; P. Mison; M. Bartholin; R. Mercier; B. Sillion; E. Geneve; P. Grenier; M.-F. Grenier-Loustalot, *Polymer* **1997**, *38*, 1439.
- (127) J. M. Pickard; E. G. Jones, *Macromolecules* **1979**, *12*, 895.
- (128) M. G. Chauser; Y. M. Rodionov; M. I. Cherkashin, *J. Macromol. Sci. Chem.* **1977**, *A11*, 1113.
- (129) T. C. Sandreczki; C. Y.-C. Lee, *Polymer Preprints* **1982**, *23*, 185.
- (130) R. J. Kushbender; T. J. Aponyi, *Proceedings of the 11th National Sampe Technical Conference, Boston, 13-15 Nov.* **1979**, 295.
- (131) I. M. Barkalov; A. A. Berlin; V. I. Gol'danskii; G. Min-Gao, *Polym. Sci. USSR* **1963**, *5*, 1025.
- (132) S. Alam; L. D. Kandpal; I. K. Varma, *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1993**, *C33*, 291.
- (133) P. M. Hergenrother ; John Wiley: Chichester, 1985; Vol. 1, pp 61-86.
- (134) B. Tan *Synthesis and Characterization of Phenylethynyl Endcapped Polyetherimide Oligomers*; Virginia Polytechnic Institute and State University: Blacksburg, 1996.

- (135) G. Odian *Principles of Polymerization*; third edition ed.; John Wiley and Sons: New York, 1991.
- (136) M. Konas; T. M. Moy; M. E. Rogers; A. R. Schultz; T. C. Ward; J. E. McGrath, *Journal of Polymer Science, Part B: Polym. Phys.* **1995**, *33*, 1429.
- (137) M. Konas; T. M. Moy; M. E. Rogers; A. R. Schultz; T. C. Ward; J. E. McGrath, *Journal of Polymer Science., Part B: Polymer Physics* **1995**, *33*, 1441.
- (138) A. J. Wnuk; T. F. Davidson; J. E. McGrath, *J. Appl., Polym. Sci.: Appl. Polym. Symp.* **1978**, *34*, 89.
- (139) A. J. Wnuk *Engineering Properties of Multiphase Block Copolymers*; Editor, Ed.; Virginia Polytechnic Institute and State University: Blacksburg, 1980.
- (140) T. F. Davidson; A. J. Wnuk; J. E. McGrath, *Polymer Preprints* **1978**, *19*, 506-513.
- (141) S. Srinivas; M. Graham; M. H. Brink; S. Gardner; R. M. Davis; J. E. McGrath; G. L. Wilkes, *Polym Eng and Sci* **1996**, *36*, 1928-1940.
- (142) J. V. Facinelli; A. E. Brink; H. L. S. Liu; S. Gardner; R. M. Davis; J. S. Riffle; M. Marrocco; S. Harding, *J. Appl Polym Sci* **1997**, *63*, 1571-1578.
- (143) J. B. Stothers *Carbon-13 NMR Spectroscopy*; Academic Press: New York, 1972.
- (144) C. J. Pouchert *The Aldrich Library of NMR Spectra*; second ed., 1983.
- (145) P. C. Hiemenz *Polymer Chemistry: The Basic Concepts*; Marcel Dekker, INC.: New York, 1984.
- (146) H. G. Barth, B. E. Boyes, C. Jackson, *Anal. Chem.*, **1996**, *68*, 445R

- (147) G. W. Meyer *Novel High Performance Thermosetting Polyimides*; Virginia Polytechnic Institute and State University: Blacksburg, 1995.
- (148) A. V. Pocius *Adhesion and Adhesives Technology, An Introduction*; Hanser Publishers: Munich, 1997.
- (149) H. M. Clearfield; D. K. McNamara; G. D. Davis *Surface Preparation of Metals*; Brinson, H. F., Ed.; ASM International: Materials Park, OH, 1990; Vol. 3-Adhesives and Sealants.
- (150) I. N. Levine *Physical Chemistry*; Third ed.; McGraw-Hill Book Company: New York, 1988.

Sue Jewel Mecham
507 Lee St.
Blacksburg, VA, 24060
Home: (540) 953-2924, Office: (540) 231-8245, Fax (540) 231-8517
sueb@vt.edu

Career Objective-Entry level industrial research and development position in polymeric materials

Core Competencies

Management, direction and training of individuals involved in organic and macromolecular synthesis and characterization research efforts, organization of research efforts to identify and achieve key objectives, excellent understanding of synthesis and structure-property relationships, excellent oral and written communication skills, experienced in the communication of technical research in a multi-disciplinary environment

Education

Ph.D., Polymer Chemistry, (GPA 3.7/4.0) Virginia Polytechnic Institute & State University, May 1997

M.S., Polymer Chemistry, (GPA - 3.7/4.0) Virginia Polytechnic Institute & State University, May, 1994

B. A. Chemistry, Virginia Polytechnic Institute & State University, May, 1991

Job Experience

Postdoctoral Associate, **National Science Foundation Science and Technology Center: High Performance Adhesives and Composites Chemistry Dept., Virginia Tech, Blacksburg, VA May 1997-Present**

- Research support of varied materials projects and written and oral communications of research projects
- Supervision and management of synthesis and characterization laboratory technicians

Graduate Research Assistant, **Ph.D. Chemistry Candidate, Virginia Tech, Blacksburg, VA Aug. 1994 - May 1997**

- Oral and poster presentations of research efforts at national and regional American Chemical Society meetings, national Adhesion Society meetings and national and international adhesive and sealant council meetings;
- Synthesis and characterization of phenylethynyl terminated poly(arylene ether sulfone)s and associated phenylethynyl mono-functional small molecules for use in molecular weight control and functionalization of poly(arylene ether)s and polyesters,
- Design and characterization of functionalized poly(arylene ether sulfone)s developed to possess optimized processability and thermal and mechanical properties for structural adhesives and composite matrices.
- Synthesis and characterization of phenylethynyl functionalized controlled molecular weight aromatic polyesters using melt acidolysis as the bulk polymerization technique,

- Preparation and exhibition of a variety of polymer synthesis experiments for A.C.S. polymer short courses for 5 years;
- Training, supervision, and management of undergraduate and graduate researchers and laboratory technicians in synthesis and characterization capacities
- Maintenance of research equipment

Graduate Research Assistant, M.S. Chem. Candidate, Virginia Tech, June, 1991-May, 1994

- Synthesis and characterization of aminopropyl terminated, controlled molecular weight, polydimethylsiloxanes through bulk polymerization for use as precursors to Polyimide-b-Polydimethylsiloxane perfectly alternating block copolymers
- Preparation of thin polymeric membranes by solution casting of dilute solutions for use in gas permeation experiments
- Installation, operation and maintenance of gas permeability measurement apparatus

Research Experience in Non-thesis Areas

- a) synthesis of **polyamides** through **interfacial** and **melt** polymerization
- b) synthesis of **polystyrene** through **living anionic** polymerization and through free-radical techniques including **emulsion**, **suspension** and **solution** polymerizations
- c) synthesis of **unsaturated polyester** by melt polymerization and subsequent curing with styrene and suitable free radical initiators
- d) synthesis and characterization of dimethylamine terminated **polydimethylsiloxane** and phenol terminated **polysulfone** precursors and subsequent copolymerization to produce **polysulfone-b-polydimethylsiloxane perfectly alternating block copolymers**
- e) synthesis of **polyamic acid** followed by thermal imidization to produce **polyimide**
- f) demonstration and discussion of endgroup analysis by **potentiometric titration**
- g) demonstration of thermal analysis by **differential scanning calorimetry**

Graduate Teaching Assistant- Virginia Tech, Aug. 1991-May 1993

- Supervision and evaluation of undergraduate organic chemistry laboratory experiments
- Optimization of microscale undergraduate organic chemistry laboratory experiments

Summer Research Scholar, NASA- Langley Research Center, Hampton, VA, June-August, 1992

- Synthesis and purification of imide containing monomers and polymers

Tutor, Virginia Tech, Aug. 1990-current

- Organic Chemistry-private and group tutoring and classroom help sessions

Undergraduate Research Assistant, Virginia Tech, June 1988-May 1989

- Synthesis and Characterization of Polyhydroxyether/ Poly(dimethylsiloxane) Copolymers,

Laboratory Technician, Virginia Tech, June 1987-May 1991

- Operation and maintenance of Gel Permeation Chromatography Equipment, purchasing and materials distribution for Dr. McGrath's research group

Awards

Recipient of Adhesive and Sealant Council graduate research scholarship, Jan.-Dec. 1995, Jan.-Dec. 1996 and Jan.-May 1997

NASA Langley Summer Scholar, June -August 1992

Recipient of departmental tuition scholarship, Jan. 1992

Recipient of undergraduate research scholarship from the Center for Adhesive and Sealant Science (CASS) at Virginia Tech, 1989-1990

Publications

- 1) S. J. Mecham, W. Harrison, Y. Sun and J. E. McGrath, Controlled Molecular Weight Amorphous Aromatic Polyester Via Melt Acidolysis, *Polymer Preprints*, **38**(2), 1997
- 2) S. J. Mecham, M. M. Bobbitt, M. E. Pallack, V. Vasudevan and J. E. McGrath, Phenylethynyl Terminated Polymers as Precursors for Structural Adhesives and Composite Matrices, *Adhesion Society Proceedings*, Hilton Head, S. C., Feb. 1997
- 3) S. J. Mecham, V. Vasudevan, S. Liu, M. B. Bobbitt, S. Srinivasan, A. C. Loos and J. E. McGrath, Phenylethynyl Arylene Ether Sulfone Matrix Resins and Oligomers: Candidates for High Temperature RTM Systems, *Polymeric Materials Science and Engineering Preprints*, Vol. **74**, 61, March, 1996
- 4) S. J. Mecham, S. Jayaraman, M. M. Bobbitt, V. Vasudevan and J. E. McGrath, Synthesis and Characterization of High Temperature Curable Poly(arylene ether) Structural Adhesive and Composite Matrices, *Adhesion Society Proceedings*, Myrtle Beach, S. C., Feb. 1996
- 5) S. J. Mecham, S. Jayaraman, Y. J. Lee, J. B. Mecham, D. J. Riley, T. E. Glass and J. E. McGrath, Synthesis and Characterization of High Temperature Curable Poly(arylene ether) Structural Adhesives and Composite Matrices, *Polymer Preprints*, vol. **36**(1), 789, 1995
- 6) S. J. Mecham, M. E. Rogers, Y. Kim, and J. E. McGrath, Gas Permeability of High Performance Homo- and Copolymers *Polymer Preprints*, **34**(2), 628, 1993
- 7) B. S. Jewel, G. Sinai-Zingde, J. S. Riffle, and J. E. McGrath, The Synthesis and Characterization of Polyhydroxyether/ Polysiloxane Copolymers, *Adhesion Society Proceedings*, Savannah, Georgia, Feb. 1990
- 8) B. S. Jewel, J. S. Riffle, D. Allison, and J. E. McGrath, Synthesis and Characterization of Telechelic Polydimethylsiloxanes with Carboxylic Acid Functionality, *Polymer Preprints*, **30**(1), 295, 1989
- 9) A. Ayambem, S. Mecham, Y. Sun and J. E. McGrath, Synthesis, Characterization and Cure Studies of Phenylethynyl-Terminated Poly(arylene ether sulphones), *Polymer Preprints*, **38**(2), 1997

- 10) M. M. Bobbitt, S. J. Mecham, V. Vasudevan and J. E. McGrath, Poly(arylene ether sulfone) Thermosetting Adhesives, *Adhesion Society Proceedings*, Myrtle Beach, SC, Feb. 1996
- 11) M. E. Rogers, T. E. Glass, S. J. Mecham, D. Rogdriques, G. L. Wilkes and J. E. McGrath, Perfectly Alternating Segmented Polyimide-Polydimethyl Siloxane Copolymers via Transimidization, *Journal of Polymer Science: Part A: Polymer Chemistry*, **32**, 2663, 1994

References

James E. McGrath, Ph.D.

University Distinguished Professor
Department of Chemistry, Virginia Polytechnic Institute and State University
Director, NSF Science and Technology Center: High Performance Polymeric Adhesives and Composites
2108 Hahn Hall, Blacksburg, VA 24061-0344
Phone: (540) 231-5976, Fax: (540) 231-8517, E-mail: jmcgrath@chemserver.chem.vt.edu

Thomas C. Ward, Professor

The Adhesive and Sealant Council Endowed Professor of Chemistry
Professor of Chemistry, Virginia Polytechnic Institute and State University
Blacksburg, VA 24061-0212
Phone: (540) 231-5867, Fax: (540)-231-8517, E-mail: tward@chemserver.chem.vt.edu

Dr. John G. Dillard

Director, Center for Adhesive and Sealant Science
Department of Chemistry, Virginia Polytechnic Institute and State University
1 Davidson Hall, Blacksburg, VA 24061-0201
Phone: (540)-231-6926, Fax: (540)-231-3971, E-mail: john.dillard@vt.edu

Dr. John W. Connell, Senior Polymer Scientist

NASA Langley Research Center, Mail Stop 226
Hampton, VA 23681-0001
Phone: (757)-864-4264, Fax: (540)-864-8312, E-mail: j.w.connell@larc.nasa.gov