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Design, Synthesis and Characterization of Novel Functional Poly(aryl ether)s

by

Sean M. MacKinnon, B. Sc.

A thesis submitted to the

Faculty of Graduate Studies and Research

in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

The Department of Chemistry

Carleton University

Ottawa, Ontario, Canada

April 2001.

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Design, Synthesis and Characterization of Novel Functional Poly(aryl ether)s

submitted by

SEAN M. MACKINNON, B.Sc.

in partial fulfillment of the requirements
for the degree of Doctor of Philosophy

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April, 2001

ABSTRACT

Modifications to monomer structure is the primary focus of this dissertation, with the intent of designing functional poly(aryl ether)s (PAEs) having novel properties. The overall objectives include: (i) to design A_2X -type monomers deviating from conventional *para, para*-substitution, suitable for polymerization through either etherification or imidization reactions and concurrently impart an inert functionality (X) allowing for post polymer grafting and crosslinking and (ii) to design active PAEs suitable for optoelectronic applications.

The synthesis and polymerization of two novel A_2X difluoroarylsulfone monomers, *N*-phenyl-3,12-bis(4-fluorobenzenesulfonyl)-5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic imide and *N*-2-pyridyl-4',4''-bis-(4-fluorobenzenesulfonyl)-*o*-terphenyl-3,6-dimethyl-4,5-dicarboxylic imide, afforded poly(aryl ether sulfone)s (PAES from 4-fluorophenyl sulfone and bisphenol A) with glass transition temperatures (T_g) ranging from 200 °C to 251 °C and no deleterious effects on solubility. Chemical transformation of the phenyl imide groups into propargyl imides through either heterogeneous base hydrolysis of the phenyl imide followed by imidization or direct transimidization of the pyridyl imide allowed for the successful preparation of thermally crosslinkable PAES. The incorporation of *o*-terphenyl moieties containing latent reactive groups has allowed for the preparation of PAES with increased T_g 's, while maintaining solubility. The thermal crosslinking of acetylene moieties affords insoluble PAES. Due to the inherent U-shape of the *o*-terphenyl monomers, macrocyclic oligomers were prepared during polymerization limiting *o*-terphenyl incorporation into the PAES backbone. An

increased tendency of macrocyclic formation was observed for the non-bridged *o*-terphenyl owing to greater rotational freedom.

The synthesis and polymerization of A₂X diamino monomer, *N*-2-hydroxyethyl-3,6-diamino-1,8-naphthalimide, gave poly(aryl ether imide)s and polyimides containing the free hydroxyl groups with *T_g*'s of 249 °C and 314 °C, respectively. Post polymerization esterification with cinnamoyl chloride afforded polymers which could be photopatterned.

The development of two new “n-doping” electrochromic bisphenols derived from 3,4,9,10-perylenetetracarboxylic dianhydride and 1,4,5,8-naphthalenetetracarboxylic dianhydride with 2-(4-aminophenyl)-2-(4-hydroxyphenyl)propane, and subsequent polymerization (with bisphenol A and either 4-fluorophenyl sulfone or 4,4'-difluorobenzophenone), afforded soluble electrochromic poly(aryl ether imide)s (PAEI). PAEIs could be spin coated onto indium-tin-oxide (ITO) surfaces and electrochemically cycled in an electrochromic sandwich cell.

Overall, this dissertation reported: (i) PAES have increased *T_g*'s upon incorporation of *o*-terphenyl subunits as a result of contributions from both the rigid helical nature and the inherent U-shape structure. (ii) Macrocyclic formation is facilitated in *o*-terphenyl subunits with increased free rotation about the central phenyl ring. (iii) Photopatternable PAEI may be prepared through the derivatization of hydroxy-containing into the corresponding cinnamate pendent polymers and (iv) “n-doping” cathodically coloring electrochromic PAEs can be prepared from electrochromic bisphenol monomers based on perylene and naphthalene diimides.

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Keep hitting the fairway,

A handwritten signature in black ink, appearing to be 'Shane', with a long horizontal flourish extending to the right.

Table of Contents

Acceptance Form	ii
Abstract	iii
Acknowledgments	v
Table of Contents	vii
List of Tables	xi
List of Figures	xii
List of Schemes	xvii
List of Symbols and Abbreviations	xviii
 CHAPTER ONE. INTRODUCTION TO POLY(ARYL ETHER)S	
 I.1 Poly(aryl ether)s	 1
I.1.1 Poly(aryl ether sulfone)s	4
I.1.2 Poly(aryl ether ketone)s	5
I.1.3 Poly(aryl ether imide)s	6
 I.2 Synthetic Routes to Poly(aryl ether)s	 7
I.2.1 Aromatic Electrophilic Substitution	8
I.2.1.1 Poly(aryl ether sulfone)s via Sulfonation	9
I.2.1.2 Poly(aryl ether ketone)s via Acylation	10
I.2.2 Aromatic Nucleophilic Substitution	11
I.2.2.1 Polymerization of Bisphenols and Dihalides	12
I.2.2.1a The “caustic” process	12
I.2.2.1b The “carbonate” process	15
I.2.2.2 Polymerization of Bisphenols and Aromatic Dinitro compounds	17
I.2.2.3 Polycondensation of Dianhydrides and Diamines	19
I.2.3 Alternative Routes to Poly(aryl ether)s	20
I.2.3.1 The Ullman Polycondensation	21

I.2.3.2 Oxidative Polymerization by the Scholl Reaction	22
I.2.3.3 Metal-Catalyzed Coupling Polymerization	22
I.2.3.4 Ring Opening Polymerization	25
I.3 Structure-Property Relationships of Poly(aryl ether)s	27
I.3.1 Monomer Structure vs. Polymer Glass Transition Temperature	28
I.3.2 Monomer Structure vs. Polymer Solubility	31
I.3.3 Monomer Structure vs. Polymer Mechanical Properties	32
I.4 Rationale and Objectives	33
I.4.1 Rationale for Conventional Structure-Property Investigation	34
I.4.2 Rationale for the Design of Active PAEs for Optoelectronic Devices	36
I.5 References	39

CHAPTER TWO : FUNCTIONAL POLY(ARYL ETHER SULFONE)S CONTAINING TETRAHYDRO[5]HELICENE SUBUNITS

II.1 Introduction	46
II.2 Monomer Synthesis and Characterization	50
II.3 Polymer Synthesis and Characterization	54
II.4 Post Polymerization Transformations and Characterization	58
II.5 Macrocyclic Oligomers	62
II.6 Structure-Property Relationships from Tetrahydro[5]helicene Incorporation	65
II.7 Conclusions	66
II.8 Experimental Section	68
II.9 References	75

CHAPTER THREE: FUNCTIONAL POLY(ARYL ETHER SULFONE)S CONTAINING *O*-TERPHENYL SUBUNITS

III.1 Introduction	76
III.2 Monomer Synthesis and Characterization	77
III.3 Polymer Synthesis and Characterization	82
III.4 Post Polymerization Reaction – Transimidization	86
III.5 Macrocyclic Oligomers	89
III.6 Potential Applications	93
III.6.1 Methods of Surface Modification	93
III.6.2 Surface Characterization	94
III.7 Structure-Property Relationships from <i>o</i>-Terphenyl Incorporation	99
III.8 Conclusions	100
III.9 Experimental Section	102
III.10 References	109

CHAPTER FOUR: FUNCTIONAL POLY(ARYL ETHER IMIDE)S DERIVED FROM A 3,6-DIAMINO NAPHTHALIMIDE

IV.1 Introduction	110
IV.2 Monomer Synthesis and Characterization	113
IV.3 Polymer Synthesis and Characterization	117
IV.4 Post Polymerization Transformations and Characterization	124
IV.6 Conclusions	131
IV.7 Experimental Section	132

IV.8 References	136
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**CHAPTER FIVE: ELECTROCHROMIC POLY(ARYL ETHER
IMIDE)S DERIVED FROM PERYLENE AND
NAPHTHALENE DIIMIDES**

V.1 Introduction	139
V.2 Monomer Synthesis and Characterization	146
V.3 Electrochemistry and Spectroelectrochemistry of Imide-Bisphenols	147
V.4 Polymer Synthesis and Characterization	151
V.5 Electrochemistry and Spectroelectrochemistry of Electrochromic Polymers	157
V.6 Investigations into Solid State Electrochromic Display Devices	162
V.7 Conclusions	166
V.8 Experimental Section	167
V.9 References	172
Contributions to Knowledge	173

List of Tables

Table	Description	Page
I.1	Pendent derivatized Udel™ Polysulfone	29
I.2	Structurally different poly(aryl ether sulfone)s from commercial bisphenols	30
II.1	Characterization of PAESs derived from A ₂ X-difluoride II-4	57
III.1	Characterization of PAESs III-4a-e derived from III-3	84
III.2	MALDI-TOF MS analysis of III-Cyc4c and III-Cyc4d	91
IV.1	Comparison of NH_2 ¹ H NMR chemical shifts of diamines	119
IV.2	Comparison of poly(aryl ether imide) derived from BPADA	121
IV.2	Comparison of polyimides derived from 6FDA	123
V.1	Characterization of perylene diimide containing poly(aryl ether imide)s	153
V.2	Characterization of naphthalene diimide containing poly(aryl ether imide)s	156

List of Figures

Figure	Description	Page
I.1	Representative of the poly(aryl ether) family	2
I.2	Glass transition (T_g) and crystalline melting points (T_m) of poly(aryl ether)s	4
I.3	Commercial poly(aryl ether sulfone)s	5
I.4	Commercial poly(aryl ether ketone)s	6
I.5	Ultem TM poly(aryl ether imide)	7
I.6	Friedel-Crafts aromatic electrophilic substitution reaction	8
I.7	Preparation of Astrel TM via polycondensation sulfonylation	9
I.8	One and two monomer routes to Victrex TM PES	10
I.9	Preparation of Stilan TM via polycondensation acylation	11
I.10	General mechanism of aromatic nucleophilic substitution reaction	12
I.11	The general “caustic” approach to poly(aryl ether)s	13
I.12	The general “carbonate” approach to poly(aryl ether)s	16
I.13	Nitro-displacement route to Ultem TM	19
I.14	Polycondensation imidization of Ultem TM	20
I.15	Oxidative polymerization by the Scholl reaction	22
I.16	Nickel-catalyzed polymerization of an aryl dichloride	23
I.17	Ni(0) coupling of aryl dichloride and subsequent post polymer nucleophilic substitution	24
I.18	Ni(0) catalyzed homocoupling of arylene bismesylates	25
I.19	Macrocyclic oligomers based on spiroindane	26
I.20	Ring-opening polymerization of cyclic (a) thioethers and (b) aryl ether ketones	27

I.21	Proposed <i>o</i> -terphenyl subunits to be incorporated into PAEs	34
I.22	Proposed A ₂ X difluorosulfone monomers based on <i>o</i> -terphenyl Subunits	35
I.23	Proposed A ₂ X-diamino monomer and polycondensation imidization	36
I.24	Proposed electroactive bisphenols and poly(aryl ether)s	37
II.1	Functional poly(aryl ether sulfone)s from direct polycondensation	47
II.2	Functionalized poly(arylene ether sulfone)s via transimidization	48
II.3	Polyimides and poly(aryl ether imide)s derived from core II-1	49
II.4	Proposed difluorosulfone monomer	49
II.5	2D ¹ H NMR NOESY spectrum of II-2	52
II.6	¹ H NMR spectra of the aromatic region of (A) II-3 and (B) II-4	53
II.7	T _g vs. mole fraction of monomer II-4 in copolymers II-5a-e	56
II.8	End-capped poly(aryl ether sulfone) II-5be	58
II.9	IR spectra (1100 – 1950 cm ⁻¹) of (a) anhydride II-3, (b) imide polymer II-5b, and (c) anhydride polymer II-6	60
II.10	DSC traces of (a) compound II-7 and polymer II-8: first scan (b) and second scan (c) at a heating rate of 10 °C/min under nitrogen	62
II.11	MALDI-TOF MS of macrocyclic oligomers from II-5b	63
II.12	GPC of (a) macrocyclic oligomers from II-5b, (b) 1 wt/vol % one pot homopolymerization and (c) 1 wt/vol % sequential addition homopolymerization	64
III.1	Non-bridged <i>o</i> -terphenyl monomer III-3 analogous to II-4	76
III.2	Reported synthesis of III-1	78
III.3	¹ H NMR spectrum of III-3 (A) full spectrum (B) aromatic region	80
III.4	UV-Vis absorption spectra of monomers III-3 and II-4	81

III.5	MM ⁺ optimized molecular conformation of III-3 (left) and II-4 (right)	82
III.6	T _g versus mole % incorporation from poly(ether sulfone)s III-4a-e derived from III-3 (circles) and poly(ether sulfone)s derived from II-4 (triangles). Dotted lines indicate the T _g range of the parent poly(ether sulfone) derived from BPA and 4-fluorophenyl sulfone.	85
III.7	¹ H NMR of III-5 from transimidization	87
III.8	¹ H NMR of III-6 from post polymer transimidization of III-4c	88
III.9	DSC traces of poly(aryl ether sulfone) III-6: (a) pre-thermal treatment (b) post-thermal treatment	89
III.10	GPC traces of copolymerization III-4d: (a) 2 h @ 254 nm. (b) 4 h @ 254 nm. (c) 12 h @ 254 nm. (d) 12 h @ 325 nm.	90
III.11	Potential route of cyclodepolymerization	92
III.12	Methods for the surface modification of ITO glass with polymer III-4d	94
III.13	Cyclic voltammogram of ferrocene	95
III.14	Cyclic voltammograms of modified ITO surfaces as working electrodes	96
III.15	SEM images under the same brightness and contrast conditions of virgin samples: bare ITO (left), III-SOP (center) and III-SSW (right)	97
III.16	SEM images under the same brightness and contrast conditions of gold coated samples: bare ITO (left), III-SOP (center) and III-SSW (right)	97
IV.1	Polyimide and poly(aryl ether imide) derived from a commercial A ₂ X-type monomer	111
IV.2	General methods employed to incorporate naphthalimides into polymers	113
IV.3	(A) ¹ H NMR spectrum of IV.2 (B) ¹³ C NMR spectrum of IV.2	116
IV.4	DSC of polymer IV-4	120

IV.5	DSC of polymer IV-5	122
IV.6	IR spectra of parent polymer IV-4 and functionalized polymer IV-6	127
IV.7	DSC scans of polymer IV-6 after UV irradiation	129
V.1	Applications of electrochromic materials	140
V.2	Generic representation of dual polymer ECD sandwich cell	141
V.3	Examples of anodically and cathodically coloring "p-doping" Polythiophenes	143
V.4	Two one electron reductions of naphthalene and perylene diimides	144
V.5	Synthesis of alternating perylene containing polyimides	145
V.6	Proposed electrochromic bisphenol monomers for polycondensation etherification	145
V.7	Cyclic voltammogram of V-1	148
V.8	Cyclic voltammogram of V-2	149
V.9	UV-Vis-NIR spectroelectrochemistry of V-1: (a) neutral, (b) -600 mv and (c) -1000 mv	150
V.10	UV-Vis-NIR spectroelectrochemistry of V-2: (a) neutral, (b) -600 mv and (c) -1000 mv	151
V.11	T_g versus mole % incorporation of V-1 (● = V-1 to V-5, ■ = V-6 to V-10)	154
V.12	T_g versus mole % incorporation of V-2. (▲ = V-11 to V-15, ◆ = V-16 to V-20)	157
V.13	Cyclic voltammogram of V-7 (dashed line) compared to V-1	158
V.14	UV-Vis-NIR spectroelectrochemistry of V-7: (a) neutral, (b) -600 mv and (c) -1000 mv	159
V.15	Cyclic voltammogram of V-20 (dashed line) compared to V-2	160
V.16	UV-Vis-NIR spectroelectrochemistry of V-20: (a) neutral, (b) -600 mv and (c) -1000 mv	161

V.17	Schematic representation of a solid state half cell in an Ottle cell	162
V.18	Ottle cell half cell construction of polymer V-5 monitoring %T at 575 nm during a voltage switch from +0.2 V to -1.0 V	163
V.19	Lifetime study all solid state ECD sandwich cell monitoring %T at 650 nm for a voltage switch between +2.5 V and -2.5 V (a) 1 st switch (b) 1000 th switch	165

List of Schemes

Scheme	Description	Page
II.1	Synthesis of tetrahydro[5]helicene based A ₂ X difluorosulfone II-4	50
II.2	Polycondensation of II-4 with BPA to give II-5a-e	54
II.3	Hydrolysis of imide polymer II-5b to anhydride polymer II-6	59
II.4	Synthesis of propargyl-imide II-7 and proposed structure from the thermal trimerization reaction	61
III.1	Synthesis of monomer III-3 (i) 2-aminopyridine, 1,2-dichlorobenzene, reflux. (ii) 4-fluorobenzenesulfonyl chloride, AlCl ₃ , nitrobenzene, 115 °C.	78
III.2	Synthesis of <i>o</i> -terphenyl containing poly(aryl ether sulfone)s	83
III.3	Model synthesis of III-5 via transimidization	86
IV.1	Synthesis of A ₂ X-diamino-hydroxy monomer IV-3	114
IV.2	Polycondensation of IV.3 with BPADA and 6FDA to give IV.4 and IV.5	118
IV.3	Post polymer esterification of IV.4 to give polymer IV.6	125
V.1	Synthesis of perylene bisphenol monomer V-1	146
V.2	Synthesis of naphthalene bisphenol monomer V-2	147
V.3	Copolymerization of V-1 containing poly(aryl ether)s	152
V.4	Copolymerization of V-2 containing poly(aryl ether)s	155

List of Symbols and Abbreviations

6FDA	2,2-hexafluoroisopropylidene diphthalic anhydride
δ	chemical shift (ppm)
BPA	bisphenol-A or 4,4'-(isopropylidene)diphenol
BPADA	2,2'-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride
CV	cyclic voltammetry
DMAc	<i>N, N</i>-dimethylacetamide
DMF	<i>N, N</i>-dimethylformamide
DMSO	dimethylsulfoxide
DSC	differential scanning calorimetry
FT-IR	Fourier transform infrared
GPC	gel permeation chromatography
HRMS	high resolution mass spectroscopy
MALDI-TOF MS	matrix assisted laser desorption ionization time of flight mass spectroscopy
MDA	4,4'-methylenedianiline
M_n	number average molecular weight
MS	mass spectrum
M_p	melting point
M_w	weight average molecular weight
η_{inh}	inherent viscosity
NMP	<i>N</i>-methyl-2-pyrrolidinone
NMR	nuclear magnetic resonance
NOESY	nuclear oberhouser effect spectroscopy

ODA	4,4'-oxydianiline
PAE	poly(aryl ether)
PAES	poly(aryl ether sulfone)
PAEK	poly(aryl ether ketone)
PAEI	poly(aryl ether imide)
PEK	poly(ether)(ketone)
PEEK	poly(ether)(ether)(ketone)
PEEKK	poly(ether)(ether)(ketone)(ketone)
P3HT	poly(3-hexyl thiophene)
PhCl	chlorobenzene
PMDA	pyromellitic dianhydride
SEC	size exclusion chromatography
S_nAr	aromatic nucleophilic substitution
TCE	1,1,2,2-tetrachloroethane
T_d	onset temperature for 5 % weight loss
T_g	glass transition temperature
T_m	crystalline melting point
TGA	thermogravimetric analysis
UV	ultraviolet
Vis	visible

CHAPTER ONE: INTRODUCTION TO POLY(ARYL ETHER)S

I.1 Poly(aryl ether)s

Poly(aryl ether)s represent a class of polymeric materials having superior properties, as they function at the highest performance levels achieved by plastics today.¹ The terms “engineering thermoplastic” and “high performance plastic” have long been used to qualitatively describe the properties of poly(aryl ether)s. The ether linkage is characteristic of this polymer family which includes poly(aryl ether ketone)s, poly(aryl ether sulfone)s, poly(aryl ether imide)s and poly(phenylene ether)s (Figure I.1).¹⁻⁹

The early development of poly(aryl ether)s stemmed from the predecessor polyarylenes, which wholly contain linked 1,4-phenylene units. Polyarylenes generally have very high melting points and undetectable glass transitions, which hinder the fabrication of polymers through conventional methods such as injection molding, extruding and casting. Through the introduction of ether linkages into the backbone, a sufficient amount of flexibility is added, improving both the solubility and processability.

Structure	Typical Uses
<p>poly(aryl ether ketone)</p>	Wire and cable insulation, radiation-resistant parts, machine parts
<p>poly(aryl ether sulfone)</p>	Medical and food-processing equipment, electrical and electronics components, camera cases, piping
<p>poly(aryl ether imide)</p>	Automotive and electronics parts, composites, wire and cable insulation
<p>poly(phenylene oxide)</p>	Telecommunications and computer equipment, automotive parts, appliance housing, electrical equipment

Figure I.1. Representative of the poly(aryl ether) family ¹

One of the most important fundamental characteristics that relates to polymer properties and the processing of amorphous polymers is the glass transition temperature (T_g). For example, polystyrene has a T_g of 100 °C and has been extensively used commercially as coffee cups because the temperature of the hot liquid will not exceed the T_g . In contrast, a rubber has a T_g below room temperature and when used as tires for automobiles, should have a T_g below – 40 °C to maintain performance levels at extremely low temperatures. In an amorphous polymer, motion is generally restricted to short range vibrations and rotations allowing the polymer to remain in a glass-like state. Upon increasing the temperature, the polymer undergoes a change from the glass-like

state to one that resembles a rubber, characteristically known as the glass transition temperature. The inherent T_g of a polymer plays a crucial role when considering a particular application, as it is important to consider whether the polymer will flow at the required temperature of processing and remain structurally intact through the temperature range of the application.

On a molecular level, the T_g is encompassed by an increase in long-range molecular motion resulting from greater rotational freedom and consequently increases in segmental motion of polymer chains. In order for the chain segments to move, the space between the atoms, defined as free volume, must increase resulting in a greater volume or a lower density of the bulk polymer. On the macroscopic level, the glass transition results in an enthalpy change which may be measured through calorimetry. When heated, the amorphous region of the polymer softens over a broad range, losing its glass-like properties as it becomes more rubber-like. The stiffness, or modulus of the polymer decreases along with changes in refractive index and thermal conductivity. If the polymer contains crystalline domains, a crystalline melting point (T_m) is observed at higher temperatures and is characteristic of the polymer losing its elastomeric properties as it melts to a flowable liquid. In general, the T_g of a semi-crystalline polymer is one half to two-thirds the value of the corresponding T_m in degree Kelvin.²

Scientists have investigated the relationship between polymer structure and T_g in order to predict polymer properties. But, the predictions are approximate at best due to the approximations in the measured values which are dependent on molecular weight, method of measurement and the morphology of the polymer. Given that T_g is a function

of rotational freedom, any structural change that restricts rotation should theoretically increase T_g . On the other hand, any variation that promotes rotation or flexibility should lower T_g .² For example, increasing the number of ether linkages in a polymer backbone compared to either ketone or sulfone linkages, results in an overall lowering of T_g (Figure I.2).¹

Figure I.2. Glass transition (T_g) and crystalline melting points (T_m) of poly(aryl ether)s¹

I.1.1 Poly(aryl ether sulfone)s

Poly(aryl ether sulfone)s are the oldest member of poly(aryl ether)s that have been successfully commercialized.⁴ The technical and commercial success of poly(aryl ether sulfone)s has stemmed from a good combination of useful properties including high thermostability, good chemical stability, high glass transition temperatures and good solubility in numerous organic solvents. The sulfone groups impart a high dipole moment to the polymer, resulting in improved glass transition temperatures. The introduction of ether groups improves the flexibility and the random or regular sequence

of different bond angles (109° for sulfone groups and 125° for ether bonds) prevents crystallization. Typical examples of commercial poly(aryl ether sulfone)s are Udel™ ($T_g = 190^\circ\text{C}$), Radel™ ($T_g = 220^\circ\text{C}$) and Victrex™ ($T_g = 223^\circ\text{C}$) (Figure I.3).¹

Figure I.3. Commercial Poly(aryl ether sulfone)s¹

I.1.2 Poly(aryl ether ketone)s

The first synthetic approach to aromatic poly(ether ketone)s via Friedel-Crafts polycondensation acylation dates back to the early 1960s,⁴ yet it took almost 20 years for the first poly(aryl ether ketone) to become commercially available. This class of poly(aryl ether)s includes PEK, PEEK and PEEKK (Figure I.4) and has found commercial application in the areas of wire and cable insulation, as well as bearings and connectors in corrosive environments. The exceptional chemical resistance, superior temperature performance, low toxic gas and smoke emission, good electrical properties, low moisture absorption and excellent hydrolysis resistance, allowed poly(aryl ether ketone)s to be exploited commercially. The primary difference between poly(aryl ether

ketone)s compared to poly(aryl ether sulfone)s is the tendency of the former to crystallize. The potential of crystallization has a great influence on synthetic reaction conditions as reduced solubility leads to lower molecular weight polymers. A structure-property relationship with respect to crystallinity may be drawn when comparing amorphous and semi-crystalline poly(aryl ether ketone)s. When the unsubstituted para-phenylene units make up the backbone of poly(aryl ether ketone)s such as PEK, PEEK and PEEKK, all display crystallinity as shown from the corresponding melting point (T_m) (Figure I.4). Through the incorporation of sp^3 -hybridized atoms, such as the central carbons found in Bisphenol-A and phenolphthalein, the tendency for crystallization can be suppressed. ⁴

Figure I.4. Commercial poly(aryl ether ketone)s

I.1.3 Poly(aryl ether imide)s

Poly(aryl ether imide)s were originally commercialized by the Dupont Company in the early 1960's and have become one of the best known engineering polymers. ² The development of the poly(aryl ether imide) known as KaptonTM, from the condensation of

pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA), led to a poly(aryl ether) that was not thermoplastic and could not be injection molded. Processability is crucial as it may limit both commercialization and application. Through the random or regular incorporation of sp^3 carbon atoms and ether linkages, poly(aryl ether imide)s with measurable T_g 's and enhanced solubilities may be obtained.¹ Further investigations by General Electric, resulted in the development and commercialization a thermoplastic poly(aryl ether imide) known as Utem™ (Figure I.5).

Figure I.5. Utem™ poly(aryl ether imide)

I.2 Synthetic Routes to Poly(aryl ether)s.

Poly(aryl ether)s were originally prepared through aromatic electrophilic substitution reactions, which led to the further development of the more conventional aromatic nucleophilic substitution in later years. The preparation of poly(aryl ether)s through non-conventional methods such as metal-catalyzed coupling reactions and ring-opening polymerizations, have also been successful. However, industry and research laboratories alike generally employ nucleophilic substitution polymerization, because it leads to more predictable polymer structures compared to electrophilic substitution

polymerization. In addition, the non-conventional methods are normally of limited scope due to strict structural demands.¹

I.2.1 Aromatic Electrophilic Substitution.

The first commercial poly(aryl ether)s were prepared through electrophilic substitution reactions. Under Friedel-Crafts conditions, a Lewis acid generates electrophilic sulfonyl ($-\text{SO}_2^+$) or acylium ($-\text{CO}^+$) ions, which reacts with activated aromatics to give sulfones or ketones, respectively (Figure I.6). The reactivity of the aromatic monomers are generally governed by substituent effects, whereby the electron donating effects of an ether linkage generally leads to high molecular weight polymer. Conversely, if electron withdrawing groups are present such that they effect the reactive site, obtaining high molecular weight may be difficult or unsuccessful.¹

Figure I.6 Friedel-Crafts aromatic electrophilic substitution reaction

I.2.1.1 Poly(aryl ether sulfone)s via Sulfonation.

In the 1960's, the 3M Company was the first to introduce commercial poly(aryl ether sulfone)s prepared through electrophilic polycondensation sulfonation with the trade name Astrel™ 360^{10, 11} (Figure I.7). The polymerization of arene sulfonyl chlorides with aromatics is usually enhanced by the presence of a Friedel-Crafts catalyst, which initially made this route industrially attractive. However, the polycondensation sulfonation method leads to defects in polymer structure owing to the formation of *ortho* structures during chain growth and chain branching through *in situ* post polymerization reactions. These defects eventually affect polymer processing and mechanical properties.

Figure I.7 Preparation of Astrel™ via polycondensation sulfonation^{10, 11}

In the same time period, the ICI group developed polycondensation sulfonation chemistry for the production of Victrex™ Polyethersulfone (PES).^{9, 12} The research efforts were focused around the use of an AB-type monomer and a pair of AA- and BB-type monomers. The two-monomer route to Victrex™ PES was preferred due to the commercial availability of the monomers. However, the resulting polymer lacked

toughness as compared to the polymer obtained through the one-monomer route due to a greater degree of chain branching (Figure I.8).

Figure I.8 One and two monomer routes to VictrexTM PES ^{9, 12}

I.2.1.2 Poly(aryl ether ketone)s via Acylation.

The first report of aromatic poly(aryl ether ketone)s involved the Friedel-Crafts acylation of isophthaloyl chloride with diphenyl ether or biphenyl in the presence of 1.5 equivalents of aluminum chloride in nitrobenzene.¹³ Similarly, *p*-phenoxybenzoyl chloride was condensed in dichloromethane at ambient temperatures, however due to poor solubility during polymerization only low molecular weight poly(aryl ether ketone)s were obtained.¹⁴ Further investigation revealed that the use of an excess of aluminum chloride aided the solubility of the growing polymer, but removal and disposal of large amounts of aluminum chloride were undesirable.^{15, 16} The initial development of StilanTM resin by the Raychem Company in the early 1970's, utilized the electrophilic polymerization of *p*-phenoxybenzoyl chloride in liquid hydrofluoric acid, catalyzed by boron trifluoride (Figure I.9).^{17, 18, 19}

Figure I.9 Preparation of StilanTM via polycondensation acylation^{17, 18, 19}

I.2.2 Aromatic Nucleophilic Substitution.

The initial development of nucleophilic approaches to poly(aryl ether)s advanced the polymers into the high performance commercial market. The investigation into nucleophilic substitution polymerization was led by Farnham and Johnson of the Union Carbide Corporation. This advancement resulted in the commercialization of PolysulfoneTM, the poly(aryl ether sulfone) generated from the bisphenate salt of Bisphenol A and 4,4'-dichlorodiphenylsulfone in dimethyl sulfoxide.^{7, 20, 21} This nucleophilic method was initially referred to as the “caustic” process, but was later developed into the “carbonate” process. The general mechanism involves the nucleophilic attack of an activated dihalide by a nucleophilic phenoxide to form an intermediate Meisenheimer complex. Upon the immediate loss of the leaving group, aromaticity is achieved and the ether linkage is secured (Figure I.10).

Figure I.10 General mechanism of aromatic nucleophilic substitution reaction

I.2.2.1 Polymerization of Bisphenols and Dihalides

The polymerization of bisphenols and dihalides initiates through the action of a suitable base on the corresponding bisphenol. The initial method was referred to as the caustic process, as it involved the use of an hydroxide base. The caustic process was improved through the use of carbonate bases allowing for much milder polymerization conditions, however each method requires optimization for the successful preparation of high molecular weight polymer.

I.2.2.1a The “caustic” process.

The nucleophilic reaction of the bisphenate of Bisphenol A with 4-chlorophenyl sulfone developed by Farnham and Johnson, has now become known as the caustic process and is a perfect example of a step-growth or condensation polymerization (Figure I.11).²¹ The approach requires the initial formation of the bisphenate salt through the

dehydration of a DMSO solution of the bisphenol and a stoichiometric amount of sodium hydroxide. The polymerization pot is then cooled to facilitate the addition of the activated dihalide and heated to 160 °C. A successful polymerization requires the optimization of a number of criteria including the choice of bisphenol, dihalide, base and solvent.

Figure I.11 The general caustic approach to poly(aryl ether)s²¹

The choice of bisphenol involves two important parameters of optimization, namely the nucleophilicity of resulting bisphenate anions and the subsequent thermal stability of the anions at polymerization temperatures. Generally, electron donating substituents *para* to the phenates increase nucleophilicity and reactivity. The presence of electron withdrawing groups generally require longer reaction times and/or higher polymerization temperatures in order to obtain an adequate molecular weight. For example, alkylidene connecting groups as in Bisphenol A usually yield very high molecular weight poly(aryl ether)s within an hour of reaction time at 160 °C. In comparison, upon polymerization with Bisphenol S, which has a sulfone group connecting to phenol rings, low molecular weight polymer results after ten hours of reaction time under the same conditions.²¹

Along with the presence of electron donating or electron withdrawing groups, the thermal stability of the bisphenate anions must be considered. The poor thermal stability of bisphenates at polymerization temperatures can compromise the stoichiometry of the reaction mixture, as well as the quality of the final product. The polymerization conditions must be air free not only to limit the presence of atmospheric moisture, but also to keep oxygen from the reaction mixture due to the rapid reaction with phenoxides leading to the severely discolored polymers and decreased molecular weight.¹

The reactivity of the dihalide must also be addressed when preparing poly(aryl ether)s. The activation of aromatic dihalides has generally been achieved through the incorporation of electron withdrawing groups. The relative effectiveness of electron withdrawing groups towards facile polymerization has been ordered as $-\text{NO}_2 \sim -\text{SO}_2 > -\text{C}=\text{O} > -\text{N}=\text{N}-$. The choice of halogen has also shown to be $\text{F} \gg \text{Cl} > \text{Br}, \text{I}$. The preparation of poly(aryl ether ketone)s most often utilizes aromatic fluorides due to the decreased electron withdrawing nature of the carbonyl functional group. The most common side reaction of aromatic halides has been subsequent hydrolysis from incompletely dehydrated polymerization mixtures. The presence of water leads to the hydrolysis of the bisphenate producing sodium hydroxide, which can lead to hydrolysis of aromatic halogen end-groups. The resulting sodium salt has decreased nucleophilicity due to the presence of electron withdrawing group, terminating polymerization and disrupting stoichiometry.^{22, 23}

The choice of base is usually based on economics which leads to sodium hydroxide over potassium hydroxide. The last criterion for a successful polymerization

involves the choice of solvent. Several factors should be considered when choosing a reaction solvent including, reactivity of monomers, solubility of the monomers and polymer, reaction temperature required to achieve high polymer and the choice of base. The caustic process generally favors the use of dimethyl sulfoxide as the solvent when preparing poly(aryl ether sulfone)s. However, the preparation of poly(aryl ether ketone)s are more difficult owing to increased crystallinity, resulting in decreases in solubility. Low molecular weight poly(aryl ether ketone)s resulted until the advent of diphenyl sulfone for use as a polymerization solvent, leading to high polymer at reaction temperatures of 300 °C. ²⁴

I.2.2.1b The “carbonate” process.

The development of milder polymerization conditions was presented by the Union Carbide Corporation through the use of alkali metal carbonates as bases for the synthesis of poly(aryl ether)s, known as the “carbonate” process. ²⁵ This method differs from the caustic process in that all monomers, reagents and solvents are charged at the start of the reaction and the process does not require the initial preparation of the bisphenate salt separately (Figure I.12). Through the carbonate process, high molecular weight polymers can be achieved without the precipitation of insoluble bisphenate salts or polar oligomers.

Figure I.12. The general “carbonate” approach to poly(aryl ether)s²⁵

Similarly, the choice of bisphenol, dihalide, base and solvent play an important role in achieving high molecular weight polymer. As in the caustic process, phenolic groups react through the corresponding phenate derivatives. The polymerization can be conducted over larger temperature ranges, where crystalline poly(aryl ether ketone)s have been kept in solution by elevating polymerization temperatures up to 335 °C. The major consideration of bisphenol reactivity centers around the thermal stability at polymerization temperatures.¹

The choice of aromatic dihalide needs consideration in the same manner as the caustic process, as the reactivity is governed by the presence of electron withdrawing substituents.

The choice of base generally yields potassium carbonate which is more soluble than sodium carbonate in *N,N*-dimethylacetamide (DMAc) or *N*-methylpyrrolidinone (NMP) and the resulting potassium phenoxides are more reactive than the corresponding sodium phenoxides. The carbonate process has been postulated to proceed through the initial formation of the potassium monophenate and potassium bicarbonate. The resulting monophenate initiates nucleophilic displacement of an activated aromatic halide and the

potassium bicarbonate disproportionates into potassium carbonate, carbon dioxide and water. The presence of an azeotropic solvent such as toluene or chlorobenzene removes the water. The use of weaker bases in the carbonate process results in a finite concentration of phenolic hydroxy groups present during polymerization which leads to the enhanced solubility of intermediate oligomeric salts facilitating the choice of solvent.²¹

The most important criteria influencing the choice of solvent remain the same compared to the caustic process. However, a greater range of solvents meet the requirements for successful polymerizations. The dipolar solvents of *N,N*-dimethylacetamide (DMAc) and *N*-methylpyrrolidinone (NMP) are most frequently used in addition to sulfolane.²⁶ The use of dimethyl sulfoxide in the carbonate process is rare, as it decomposes in the presence of acidic phenolic end groups resulting in a stoichiometric offset and overall poor polymer quality.¹

1.2.2.2 Polymerization of Bisphenols and Aromatic Dinitro Compounds

As previously described, the onset of polyimides as one of the largest families of engineering thermoplastics initiated from research in the mid-1950's at the Dupont Company. The development of KaptonTM allowed for numerous high temperature applications, yet it was not processable.²⁷ The advent of nitro-displacement reactions led to the injection moldable poly(aryl ether imide) commercially known as UltemTM. The General Electric Company introduced UltemTM commercially in 1982 after numerous years of research and process development.²⁸

The preliminary studies of the nucleophilic displacement of aromatic nitro groups at the GE company led to the development of commercial, thermoplastic poly(aryl ether imide)s. The facile displacement of both 3- and 4-nitro-*N*-phenylphthalimides with phenoxides under the “caustic process” produced the corresponding phenyletherimides in excellent yields. The corresponding chloro- and fluoro-phenylphthalimides were found to be reactive, but not to the extent of the nitro derivatives. The preparation of bis-nitro-bis-imides allowed for the application of this chemistry as a potential route to Ultem™ poly(aryl ether imide). The anhydrous bis-phenoxide salt may be polymerized with the dinitro monomer under mild conditions in a dipolar aprotic solvent such as dimethyl sulfoxide or *N,N*-dimethylformamide (Scheme I.6).^{28,29,30} This method gives high molecular weight polymer, yet is not favored for commercial production. The resulting polymers contain phenolic and nitro end groups leading to a diminished thermo-oxidative stability at the temperatures required for melt processability. The polymerization system must be kept under anhydrous conditions due to the potential hydrolysis of the nitro-imide to its precursor nitro-amic acid, which does not undergo displacement and offsets the overall stoichiometry.²⁸

Figure I.13 Nitro-displacement route to UltemTM 28, 29, 30

I.2.2.3 Polycondensation of Dianhydrides and Diamines.

An alternative synthesis to poly(aryl ether imide)s may be employed based on traditional polyimide synthesis. The condensation of dianhydrides and diamines through the intermediate poly(amic acid), leads to polyimides via the imide formation. Through the use of suitable ethers containing dianhydrides and/or diamines, a variety of poly(aryl ether imide)s may be prepared from the multitude of monomers generally used in the preparation of commercial polyimides (Figure I.14). This is the preferred method over the polycondensation etherification route using a bisphenoxide and bis-nitro-bis-imide.³¹ The commercial preparation of UltemTM is centered around the nitro-displacement of 4-nitro-*N*-substituted phthalimides with the disodium salt of Bisphenol-A, to yield the bis(ether imide). The bis(ether imide) may be hydrolyzed in aqueous sodium hydroxide leading to the tetra-acid, where upon dehydration gives the bis(ether anhydride). The

advantage of this method over the caustic polymerization conditions is that the end groups can be readily converted to thermo-oxidative stable imides.

Figure I.14 Polycondensation imidization of Utem™ 31

I.2.3 Alternative Routes to Poly(aryl ether)s

Throughout the history of poly(aryl ether) synthesis, alternative methods have been investigated resulting in a variety of pathways not conventionally defined by nucleophilic or electrophilic classifications. The classification of conventional or alternative methods has not been based on the importance of one method over another, as one of the alternative methods to poly(aryl ether)s is commercially practiced. In the early 1900's, Ullman's early work involved the synthesis of aryl ethers and the formation of aryl-aryl bonds through metal catalyzed dihaloaryl coupling. The later development of

the Scholl reaction for the synthesis of poly(aryl ether)s through a radical-cation polymerization, has added to the list of potential synthetic routes. In addition, recent polymerization methods based on the ring opening of macrocycles have surfaced, yet have not been exhausted due to their high demand of structural requirements.¹

I.2.3.1 The Ullman Polycondensation

The polymerization of dihaloaromatics with bisphenates through the Ullman reaction has not been extensively implemented in the preparation of poly(aryl ether)s. The Ullman reaction involves the displacement of a halide with a reactivity opposite to that of nucleophilic displacement; $I > Br > Cl > F$. The main disadvantage to this route leading to commercialization is based on the use of very expensive halides in order to achieve acceptable molecular weights. An early report outlined the preparation of both low molecular weight Polysulfone from the bisphenate salt of Bisphenol A and 4,4'-dibromodiphenylsulfone and the poly(aryl ether ketone) from the corresponding dichlorobenzophenone, in the presence of cuprous oxide in dimethyl sulfoxide at 153 °C.

³² There is a potential for high molecular weight polymer formation, however when weighed against the facile nucleophilic displacement of the same bisphenate salt with the less expensive 4,4'-dichlorodiphenylsulfone, the Ullman polymerization falls short and has not been widely used.

I.2.3.2 Oxidative Polymerization by the Scholl Reaction

The use of the Scholl reaction has led to the successful preparation of poly(aryl ether sulfone)s and poly(aryl ether ketone)s.^{33, 34} The reaction may be described as the elimination of two hydrogen atoms through the formation of an aryl-aryl bond in the presence of a Friedel-Crafts catalyst such as ferric chloride (Figure I.15). The mechanism of the radical-cation polymerization has been accepted to initiate through the one electron oxidation of the monomer by the action of ferric chloride.^{35, 36} The most successful radical-cation polymerizations have involved the use of monomers containing the naphthoxy moiety, owing to their facile oxidation. The general use of this polymerization method was investigated for commercial preparation without success due to the relatively low molecular weights obtained even after prolonged reaction times of 48 h.³⁷

Figure I.15 Oxidative polymerization by the Scholl reaction^{35, 36}

I.2.3.3 Metal-Catalyzed Coupling Polymerization

The development of new methods of preparing poly(aryl ether sulfone)s and poly(aryl ether ketone)s has led to nickel(0) promoted coupling³⁸⁻⁵⁰ of aryl dihalides

based on the earlier research on the corresponding mono functional aryl halides.^{38,39} For example, the preparation of Radel RTM offers an alternative route to polymers normally prepared by nucleophilic methods (Figure I.16). The conditions effecting polymerization have been investigated in order to assess the commercial feasibility of this reaction.³⁸ The polymerization may be performed with catalytic amounts of zero valent nickel, under inert atmosphere in an anhydrous aprotic solvent, such as *N,N*-dimethylacetamide. In addition to catalytic amounts of nickel, large amounts of triphenylphosphine and an excess of zinc metal are required at polymerization temperatures around 70 °C. The preparation of high molecular weight polymer is dependent on the solubility of both the monomer and corresponding polymer in the reaction solvent. The major disadvantage to the commercialization of this process is based on the necessity to separate the catalyst components from the collected polymer.³⁸

Figure I.16 Nickel-catalyzed polymerization of an aryl dichloride

Recently Sheares et al. have reported functional polyphenylenes via $\text{Ni}(0)$ catalyzed coupling of bis(aryl chlorides) as a flexible route to a variety of high

performance materials.⁴⁰⁻⁴⁴ For example, poly[2-(4-fluorobenzenesulfonyl)-1,4-phenylene] was prepared from 4'-fluoro-2,5-dichlorodiphenyl sulfone allowing for further derivatization via nucleophilic substitution of the activated fluorophenyl sulfone pendent group (Figure I.17).

Figure I.17 Ni(0) coupling of aryl dichloride and subsequent post polymer nucleophilic substitution

Metal-catalyzed coupling polymerization have been employed by Percec et al through the synthesis of polyarylenes via Ni(0)-catalyzed homocoupling of arylenebismesylates.⁴⁵⁻⁴⁹ Bisphenols containing a variety of functional groups including isopropylidene, ether, ketone and sulfone, lead to the bismesylates through treatment with methanesulfonyl chloride. Polymerizations were typically performed in THF at 67 °C, yielding molecular weights below 10 000 g/mol and of limited solubility. The polymerizations are not always successful in obtaining high molecular weight due to the

use of optimum polymerization temperatures of 70 to 90 °C, which is not adequate to dissolve the growing polymer leading to precipitation of low molecular weight polymer.⁵⁰

Figure I.18 Ni(0)-catalyzed homocoupling of arylene bismesylates

I.2.3.4 Ring-Opening Polymerization

An alternative to preparing poly(aryl ether)s common to poly(aryl ether sulfone)s,^{51, 52} poly(aryl ether ketone)s^{52, 54} and poly(aryl ether imide)s,^{53, 54} is based on the ring opening of suitable macrocyclic oligomers. The advantages of ring-opening polymerization include improved processability, as viscosities are lower for macrocyclic oligomers, and the reduction of large amounts of salts and solvents present during bulk polymerizations. However, the underlying economic factor generally required in the preparation of the prerequisite macrocycles, has hindered commercialization. Spiroindane based macrocyclic oligomers containing sulfone, ketone and imide functionalities have been prepared in high yields, due to the unique tendency of spiroindane monomers to form cyclics (Figure I.19). Moreover, macrocyclics from more conventional linear monomers have also led to cyclics under high dilution conditions. The subsequent ring opening of sulfone and ketone containing macrocyclic oligomers

may be facilitated by catalytic amounts of the disodium salt of Bisphenol A or cesium fluoride at temperatures ranging from 300 – 380 °C.^{55,56} However, the corresponding imide containing macrocyclics were very high melting and sparingly soluble, limiting investigations into solution and melt polymerization.⁵⁴

Figure I.19 Macrocyclic oligomers based on spiroindane⁵²⁻⁵⁴

Recently, Hay et al. have reported a series of macrocyclic oligomers suitable for ring-opening polymerization based on cyclic thioethers⁵⁶⁻⁶⁴ and aryl ethers containing ketone,⁶⁵⁻⁶⁹ phthalazine,⁶⁹ isoquinoline,⁶⁹ phenylphosphine oxide⁷⁰ and tetraphenylbenzene⁷¹ moieties. For example, cyclic thioethers were prepared through the quantitative chemical reduction of the corresponding cyclic sulfoxides. The subsequent ring-opening polymerization at elevated temperatures, in the presence of catalytic amounts of 2,2'-dithiobis(benzothiazole) (DTB), led to high molecular weight poly(aryl ether ether sulfide)s⁵⁹ (Figure I.20a). Furthermore, the synthesis of cyclic aryl ether

ketones from 1,2-bis(4-fluorobenzoyl)benzene and various bisphenols afforded high molecular weight polymers at temperatures up to 340 °C in the presence of CsF (Figure I.20b).⁶⁸

Figure I.20 Ring-opening polymerization of cyclic (a) thioethers (b) aryl ether ketones

I.3 Structure-Property Relationships of Poly(aryl ether)s

Throughout the development of poly(aryl ether)s, basic research has primarily focused on structure-property relationships. The ability of predicting bulk polymer properties is of great importance as the shift towards tailoring of the polymer properties for specific applications become the norm. The properties of interest generally include the T_g , solubility and mechanical properties and the relation to polymer structure. The T_g of a polymer dictates the temperature range suitable for application. The solubility, along

with viscosity, sheds light on polymer processability and the mechanical properties relate to conditions of failure throughout a particular application.

I.3.1 Monomer Structure vs. Polymer Glass Transition Temperature

The T_g of a polymer may be related to the overall rotational freedom and flexibility available to the polymer backbone due to either inter-chain steric interactions or stronger bonding interactions. For example, the presence of long alkyl groups within the polymer backbone usually results in a lowered T_g due to increases in flexibility. Conversely, the incorporation of a rigid aromatic moiety leads to a greater T_g and limited flexibility. The introduction of pendant groups such as methyl groups generally leads to a higher T_g due to increased restrictions on the free rotation of polymer chains.^{20, 73} The presence of pendant groups allowing for polymer inter-chain interactions results in greater increases in glass transition temperatures compared to functional groups that are limited to steric interactions alone.⁷²⁻⁷⁷ For example, the presence of carboxylic acid groups leads to increased inter-chain interaction through hydrogen bonding and the greater number of carboxylic acid groups present, the greater number of potential interactions resulting in higher T_g .⁷⁶ A series of derivatized UdelTM polysulfones are listed in Table I.1, giving rise to the varying changes in T_g induced through pendant groups.

Table I.1 Pendant derivatized Udel™ Polysulfone

<p>$T_g = 190\text{ }^{\circ}\text{C}^{72}$</p>	<p>$T_g = 178\text{ }^{\circ}\text{C}^{73}$</p>
<p>$T_g = 195\text{ }^{\circ}\text{C}^{74}$</p>	<p>$T_g = 235\text{ }^{\circ}\text{C}^{20}$</p>
<p>$T_g = 138\text{ }^{\circ}\text{C}^{75}$</p>	<p>$T_g = 210\text{ }^{\circ}\text{C}^{76}$</p>
<p>$T_g = 205\text{ }^{\circ}\text{C}^{20}$</p>	<p>$T_g = 220\text{ }^{\circ}\text{C}^{76}$</p>
<p>$T_g = 191\text{ }^{\circ}\text{C}^{77}$</p>	

The T_g of a polymer may also be tailored through the variation in monomer substitution patterns. The commercial availability of structurally different monomers suitable for poly(aryl ether) synthesis, greatly influenced the initial monomer structure vs. T_g investigations. Structural variations of bisphenol monomers have dominated the research due to increased availability. An example of the effect of bisphenol structure on

the thermal properties of a series of structurally different poly(aryl ether sulfone)s may be observed throughout the literature (Table I.2).

Table I.2 Structurally different poly(aryl ether sulfone)s from commercial bisphenols.

$\left[\text{O}-\text{Ar}-\text{O}-\text{C}_6\text{H}_4-\text{SO}_2-\text{C}_6\text{H}_4-\text{O} \right]$			
Ar	T _g (°C)	Ar	T _g (°C)
184-195 ²⁰		227 ⁷⁹
203 ⁷⁸		221 ⁷⁹
170 ⁷⁸		215 ⁷⁹
171 ⁷⁸		281 ⁸⁰
221 ⁷⁸		275 ⁸²
280 ⁸¹		

For example, poly(aryl ether sulfone)s derived from 1,4-hydroquinone and 4,4'-biphenol have a T_g of 203 °C and 221 °C, respectively.⁷⁸ The structurally modified ortho- and meta- hydroquinones destroy the overall chain linearity of the para-para- substituted hydroquinone, resulting in an approximate 30 °C decrease in T_g.⁷⁸ Furthermore, the

incorporation of fused ring systems such as naphthalene into the polymer main chain, also follow a similar trend. The general trend has been that the more linear the bisphenol monomer, the greater the T_g . For example, the measured T_g 's of PAES derived from 2,6-substituted naphthalenes are higher compared to the 1,6- and 2,7-substituted derivatives.

^{79, 80} Structural variations of Bisphenol-A have led to fluorenone and phenolphthalein based bisphenols. The overall polymer backbone has a larger free volume due to increased distances between polymer chains, which is accompanied by increases in aromaticity and results in a much greater T_g .^{81, 82}

1.3.2 Monomer Structure vs. Polymer Solubility

The importance of polymer solubility is critical as many polymer properties are related to molecular weight and throughout a polymerization reaction, the growing polymer solubility decreases as inter-chain interactions increase. The processability of a polymer is also related to solubility and designing polymer structures to facilitate processing is required. Generally, the solubility of PAEs follow similar trends to that of monomers in that “like” solvents dissolve “like” compounds. Polar aprotic solvents usually dissolve PAEs whereas, non-polar solvents such as hydrocarbons do not. However, the polymer structure plays a critical role. The process of dissolving a polymer compared to low-molecular-weight compounds is vastly different due to the dimensions of solvent and polymer molecules.¹ Solutions generally occur through a two step process, where solvent molecules diffuse into a polymer matrix to give a swollen gel,

followed by the breaking up of the gel allowing for molecules to disperse into a true solution.¹

Overall the opposite trend to that of T_g is observed, where the greater the polymer flexibility or free volume, the greater the solubility. In some cases both increases in solubility and T_g can be achieved through pendent group functionalities such as methyl and phenyl groups, however, in most instances aromatic character in the polymer backbone induces rigidity and decreases the overall polymer solubility.¹ For example, the polymerization of 4-chlorophenylsulfone with BPA via the carbonate process may be done in DMAc, however upon substituting hydroquinone for BPA, sulfolane or NMP at lower concentrations must be used and the polymer must be filtered hot to prevent crystallization.²⁶

I.3.3 Monomer Structure vs. Polymer Mechanical Properties

The mechanical properties of commercial polymers are of fundamental interest because regardless of use, all polymers must exhibit a specified range of mechanical properties suitable for an application. The mechanical properties of polymers describe how much stress a sample can withstand before failure. Poly(aryl ether sulfone)s are generally amorphous and exhibit high dimensional stability at elevated temperatures. This mechanical property is sensitive to polymer structure and provided that the molecular weight is above the entanglement threshold, the main influences on polymer toughness are high polarity and an all para-substitution pattern.⁸ The effect of the repeat unit structure on the toughness of poly(aryl ether sulfone)s was reported by Attwood et

al, through the correlation of notched impact strength as a measure of toughness.⁷⁸

Through variation in the bisphenol structure, a series of structurally different PAESs were prepared from 4-chlorophenylsulfone. As compared to UdelTM, PAESs containing 1,2- or 1,3-substituted phenylene rings had a marked decrease in toughness. The inclusion of an asymmetrically substituted 4-naphthalene-4-phenylene sulfone unit, also led to an observed decrease in toughness, whereas the incorporation of ketone linkages or paraphenylene groups both led to substantial increases in toughness. In general, the higher the chain symmetry of the polymer, the higher the toughness.⁷⁸

I.4 Rationale and Objectives

Throughout the history of poly(aryl ether) research, the focus has changed from slight monomer structure variations, to the tailoring of polymer structure for a particular application. The ability of predicting the desired polymer properties has become critically important with the onset of new potential applications.

As evident from the previous structure-property relationships described, the general problems of poly(aryl ether)s also plague most high temperature polymer families. Namely, as the T_g of a polymer is increased, decreases in solubility and mechanical properties usually result due to the introduction of rigid aromatic groups or asymmetry into the polymer backbone. Also, the conventional uses of PAEs continue as passive materials, yet tailoring these polymers for modern active electronic applications has begun.⁸³⁻⁸⁶

I.4.1 Rationale for Conventional Structure-Property Investigation

In order to further probe the effects of monomer structure on polymer properties, *o*-terphenyl units and subsequent incorporation into poly(aryl ether)s are proposed (Figure I.21). Through the incorporation of *o*-terphenyl units into the polymer mainchain, an increase in the T_g is expected, while the solubility should not be adversely effected. However, it is also expected that increasing amounts of *o*-terphenyl character will have deleterious effects on mechanical properties due to the inherent structure that deviates from linear para-phenylene substitution. A comparison of bridged and non-bridged *o*-terphenyl subunits should allow for a comprehensive analysis of the overall properties induced through variations in structure.

Figure I.21 Proposed *o*-terphenyl subunits to be incorporated into PAEs

To accommodate for losses in mechanical properties and to broaden the scope of application, a latent functionality is proposed that should allow for facile post polymerization reactions and greater control over mechanical properties through crosslinking of grafted polymers. This approach has been investigated by Hay et al, through the incorporation of linear phenyl imidoarylenes into PAEs through the corresponding bisphenol.⁸³ The subsequent transimidization of the parent phenyl imide

with hydrazine, allowed for pendent amino groups to be introduced and further derivatized.

The use of an *o*-terphenyl based monomer containing a latent anhydride allowing for further grafting and crosslinking is proposed. These monomers are referred to as an A₂X-type monomers, where the “X” functionality represents a latent group inert to polymerization conditions, yet labile to post polymer grafting and crosslinking. The design of an A₂X-type monomer suitable for polymerization requires the initial consideration of which polymerization method is best suited for such an endeavor. The choice of nucleophilic polycondensation is appropriate, as electrophilic methods generally lead to uncontrollable structural defects. Due to the strict guidelines required for a successful nucleophilic polycondensation etherification, the availability of suitable dihalide monomers are scarce. Therefore, the synthesis and polymerization of following A₂X-type difluorosulfone monomers based on *o*-terphenyl subunits are proposed (Figure I.22).

Figure I.22 Proposed A₂X difluorosulfone monomers based on the *o*-terphenyl subunit

The extension of A₂X-type monomers allowing for the preparation of functionalizable poly(aryl ether imide)s and polyimides will be investigated through the design of a suitable naphthalimide-based diamine monomer (Figure I.23). The structure-property relationships arising from polymers derived from commercially available dianhydrides should have a similar trend to that of the *o*-terphenyl monomers due to the nonlinear structure and will be compared to both commercial and reported polymers containing similar subunits. The derivatization of the latent “X” functionality through the incorporation of a cinnamate is proposed and will lead to photocurable poly(aryl ether imide)s. The proposed route to photocurable PAEIs is as follows (Figure I.23).

Figure I.23 Proposed A₂X-diamino monomer and polycondensation imidization

I.4.2 Rationale for the Design of Active PAEs for Optoelectronic Devices.

The optoelectronic application of choice for preliminary investigations of the design of active PAEs is that of electrochromic devices. An electrochromic device is comprised of a transparent anode and cathode, each supporting a thin electrochromic material, which are sandwiched between a gel electrolyte. There are three main classes of

electrochromic materials including metal oxides, organic dyes and conjugated polymers. The class of conjugated polymers has been dominated by “p-doping” materials, which undergo an oxidation from the neutral state such as poly(thiophene)s, poly(aniline)s and poly(pyrrole)s.⁸⁷ The overall lack of “n-doping” electrochromic polymers will be addressed through the development of “n-doping” monomers suitable for polymerization. Why use PAEs as an active material? Owing to the exceptional properties, i.e. chemical resistance, hydrolytic stability, transparency, dimensional stability at elevated temperatures owing to high T_g 's and good solubility facilitating fabrication, PAEs are a good choice as parent polymers. The downfall is that PAEs are insulating by nature and do not facilitate conduction due to the overall lack of extended linear conjugated pathways found in conducting polymers. The diimides of perylene and naphthalene are known to change color upon reduction⁸⁸⁻⁹⁰ and are the proposed routes to electrochromic monomers after derivatization into suitable bisphenols (Figure I.24).

Figure I.24 Proposed electroactive bisphenols and poly(aryl ether)s

In summary, the overall objectives of this thesis include,

- (1) the synthesis and subsequent polymerization of A₂X-type *o*-terphenyl based dihalide monomers yielding functional poly(aryl ether sulfone)s.**
- (2) the determination of the structure-property relationships arising from the incorporation of *o*-terphenyl subunits into poly(aryl ether sulfone)s.**
- (3) the extension of A₂X-type monomer as route to preparing functional poly(aryl ether imide)s.**
- (4) the investigation of poly(aryl ether)s as active materials in optoelectronic devices.**

I.5 References

- 1) Cotter, R. J. *Engineering Plastics: Handbook of Polyarylethers*; 1st ed.; Gordon and Breach Publishers: United States, 1995.
- 2) Stevens, M. *Polymer Chemistry: An Introduction*; Oxford University Press: New York, 1990.
- 3) Clagett, D. C. *Engineering Plastics*, In: *Encyclopedia of Polymer Science and Engineering*; Mark, H. F., Bikales, N.M., Overberger, C.G., Menges, G., Ed.; John Wiley & Sons: Toronto, 1988; Vol. 6, pp 94-131.
- 4) Kricheldorf, H. R. "Aromatic Polyethers", In: *Handbook of Polymer Synthesis Part A*; ; Marcel Dekkar Inc.: New York, 1991, pp 545-615.
- 5) Smith, C. P. *Chemtech* 1988, May, 290-291.
- 6) Rseich, M. S. *Chemical and Engineering News* 1989, Sept 4, 21-49.
- 7) Harris, J. E., Johnson, R. N. "Polysulfones", In: *Encyclopedia of Polymer Science and Engineering*; ; Mark, H. F., Bikales, N.M., Overberger, C.G. Menges, G., Ed.; John Wiley & Sons: New York, 1988; Vol. 13, pp 196-211.
- 8) Tickton, A. E.-W., K "Poly(ether Sulfone)s - Properties Applications and Trends", In: *Polymeric Materials Encyclopedia*; ; Salamone, J. C., Ed.; CRC Press: New York, 1996; Vol. 8, pp 5936-5948.
- 9) Parodi, F. "Polysulfones", In: *Comprehensive Polymer Science*; ; Allen, G., Bevingtin, J.C., Ed.; Pergamon: Oxford, 1989; Vol. 5, pp 561-591.
- 10) Vogel, H. A. *J. Polymer Sci: A-1*, 1971, 8, 2035.

- 11) Rose, J. B. in *"High Performance Polymers: Their Origins and Development"*, Elsevier; 1986, p. 169.
- 12) Rose, J. B. *Polymer*, 1974, 15, 456.
- 13) Bonner, W. H., U.S. Pat. 3065205 (1962).
- 14) Goodman, I., McIntyre, J. E. and Russell, W., Brit Pat. 971227 (1964).
- 15) Niume, K.; Toda, F.; Uno, K.; Hasegawa, M.; Iwakura, Y., *J. Polym. Sci., Polym. Chem. Ed.*, 1982, 20, 1965.
- 16) Jansons, V., and Gors, H. C. U.S. Pat. 4709007 (1987).
- 17) Rose, J. B. in *"High Performance Polymers: Their Origins and Development"*, Elsevier; 1986, p. 187.
- 18) Rose, J. B., in "Recent Advances in Mechanistic and Synthetic Aspects of Polymerization," Fontanille, M.; Guyot, A. Ed.; D. Reidel Publishing Co., 1987. p. 207.
- 19) Staniland, P. A., in "Comprehensive Polymer Science," Vol. 5, Chapter 29, G. Allen. Ed.; Pergamon Press; 1989. p 483.
- 20) Johnson, R. N.; Farnham, A. G.; Clendinning, R. A.; Hale, W. F; Merriam, C. N., *J. Polymer Sci. A-1*, 1967, 5, 2375.
- 21) Clendinning, R. A., Farnham, A. G., and Johnson, R. N., "Development of Polysulfone and Other Polyarylethers" in *"High Performance Polymers: Their Origin and Development"*. Seymour, R. B.; Kirshenbaum, G. S., Ed.; Elsevier; 1986. p 149.

- 22) Rose, J. B., "Discovery and Development of the VictrexTM Polyarylethersulfones" in "High Performance Polymers: Their Origins and Development", Seymour, R. B.; Kirshenbaum, G. S., Ed.; Elsevier; 1986. p 169.
- 23) Newton, A. B.; Rose, J. B., *Polymer*, **1972**, *13*, 465.
- 24) Atwood, T. E.; Dawson, P. C.; Freeman, J. L.; Hoy, L. R. J.; Rose, J. B.; Staniland, P. A., *Polymer*, **1981**, *22*, 1096.
- 25) Clendinning, R. A., Farnham, A. G., Zutty, N. L., and Priest, D. C., Can. Pat. 847, 963 (1970).
- 26) Viswanathan, R.; Johnson, B. C.; McGrath, J. E., *Polymer*, **1984**, *25*, 1827.
- 27) Cotter, R. J., and Matzner, M., Chapter 1 in "Ring Forming Polymerizations", Part B Vol. 2, Academic Press, New York, 1972.
- 28) Wirth, J. G., in "High Performance Polymers: Their Origins and Development", Seymour, R. B.; Kirshenbaum, G. S., Ed.; Elsevier; 1986. p. 195.
- 29) Takekoshi, T.; Wirth, J. G.; Heath, D. R.; Kachanowski, J. E.; Manello, J. S.; Webber, M. J., *J. Polym. Sci.: Polym. Chem. Ed.*, **1980**, *18*, 3069.
- 30) White, D. M.; Takekoshi, T.; Williams, F. J.; Relles, H. M.; Donahue, P. E.; Klopfer, H. J.; Loucks, G. R.; Manello, J. S.; Matthews, R. O.; Schluez, R. W., *J. Polym. Sci.: Polym. Chem. Ed.*, **1981**, *19*, 1635.
- 31) Takekoshi, T.; Kochanowski, J. E.; Manello, J. S.; Webber, M. J., *J. Polym. Sci.: Polym. Chem. Ed.*, **1985**, *23*, 1759.
- 32) Jennings, B. E.; Jones, M. E. B.; Rose, J. B., *J. Polym. Sci.: C*, **1967**, *16*, 715.
- 33) Percec, V.; Nava, H., *J. Polym. Sci.: Polym. Chem.*, **1988**, *26*, 783.

- 34) Percec, V.; Wang, J. H.; Oishi, Y.; Feiring, A. E., *J. Polym. Sci.: A : Polym. Chem.*, **1991**, *29*, 965.
- 35) Percec, V.; Wang, J. H., *Polym. Preprints*, **1991**, *32(1)*, 391.
- 36) Percec, V.; Okita, S.; Wang, J. H., *Macromolecules*, **1992**, *25*, 64.
- 37) Percec, V.; Wang, J. H.; Oishi, Y., *J. Polym. Sci. Polym. Chem.*, **1991**, *29*, 949.
- 38) (a) Colon, I.; Moresea, L. M.; Kwiatkowski, G. T., U.S. Pat. 4,263,466 (1981). (b) Colon, I.; Kwiatkowski, G. T., *J. Polym. Sci. Polym. Chem.*, **1990**, *28*, 367.
- 39) Colon, I.; Kelsey, D. R., *J. Org. Chem.*, **1986**, *51*, 2627.
- 40) Phillips, R. W.; Sheares, V. V.; Samulski, E. T.; Desimore, J. M., *Macromolecules*, **1994**, *27*, 2354.
- 41) Pasquale, A. J.; Vonhort, T. K.; Sheares, V. V., *Polym. Preprints*, **1997**, *38(1)*, 170.
- 42) Wang, J.; Vonhort, T. K.; Sheares, V. V., *Polym. Preprints*, **1997**, *38(2)*, 263.
- 43) Pasquale, A. J.; Sheares, V. V., *J. Polym. Sci. Polym. Chem.*, **1998**, *36*, 2611.
- 44) Bloom, P.; Sheares, V. V., *Polym. Preprints*, **1999**, *40(2)*, 567.
- 45) Percec, V.; Zhao, M.; Bae, J. -Y.; Asandei, A. D.; Hill, D. H., *Polym. Bull.*, **1997**, *38*, 515.
- 46) Percec, V.; Bae, J. -Y.; Zhao, M.; Hill, D. H., *Macromolecules*, **1995**, *28*, 6726.
- 47) Percec, V.; Bae, J. -Y.; Zhao, M.; Hill, D. H., *J. Org. Chem.*, **1995**, *60*, 1066.
- 48) Percec, V.; Bae, J. -Y.; Hill, D. H., *J. Org. Chem.*, **1995**, *60*, 1060.
- 49) Percec, V.; Bae, J. -Y.; Zhao, M.; Hill, D. H., *J. Org. Chem.*, **1995**, *60*, 176.
- 50) Ueda, M.; Ichikawa, F., *Macromolecules*, **1990**, *23*, 926.

- 51) Colquhoun, H. M.; Dudman, C. C.; Thomas, M.; O'Mahony, C. A.; Williams, D. J., *J. Chem. Soc., Chem. Commun.*, **1990**, 336.
- 52) Cella, J. A.; Fukuyama, J.; Guggenheim, T. L., *Polym. Preprints*, **1989**, 30(2), 142.
- 53) Cella, J. A.; Talley, J. J.; Fukuyama, J., *Polym. Preprints*, **1989**, 30(2), 581.
- 54) Mullins, M. J.; Woo, E. P.; Chen, C. C.; Murray, D. J.; Bishop, M. T.; Balon, K. E., *Polym. Preprints*, **1991**, 32(2), 174.
- 55) Mullins, M. J.; Woo, E. P.; Bishop, M. T.; Galvan, R.; Gorman, D. B.; Chamberlin, T. A., *Polym. Preprints*, **1992**, 33(1), 414.
- 56) Ding, Y.; Hay, A. S., *Macromolecules*, **1996**, 29, 6386.
- 57) Wang, Y. -F.; Hay, A. S., *Macromolecules*, **1996**, 29, 5050.
- 58) Ding, Y.; Hay, A. S., *Macromolecules*, **1996**, 29, 4811.
- 59) Wang, Y. -F.; Hay, A. S., *Macromolecules*, **1996**, 30, 182.
- 60) Ding, Y.; Hay, A. S., *Macromolecules*, **1996**, 30, 2527.
- 61) Ding, Y.; Hay, A. S., *Polymer*, **1997**, 38, 2239.
- 62) Ding, Y.; Hay, A. S., *J. Polym. Sci. Polym. Chem.*, **1997**, 35, 2961.
- 63) Tsuchida, E.; Miyatake, K.; Yamamoto, K.; Hay, A. S., *Macromolecules*, **1998**, 31, 6469.
- 64) Meng, Y.; Hay, A. S., *J. Polym. Sci. Polym. Chem.*, **1999**, 74, 3069.
- 65) Jiang, H.; Chen, T.; Bo, S.; Xu, J., *Macromolecules*, **1997**, 30, 7345.
- 66) Gao, C.; Hay, A. S., *Polymer*, **1995**, 36, 4141.
- 67) Wang, Y. -F.; Chan, K. P.; Hay, A. S., *J. Appl. Polym. Sci.*, **1996**, 59, 831.
- 68) Chan, K. P.; Wang, Y. -F.; Hay, A. S., *Macromolecules*, **1995**, 28, 653.

69) Chan, K. P.; Wang, Y. -F.; Hay, A. S.; Hronowski, X. L.; Cotter, R. J.

Macromolecules, **1995**, *28*, 6705.

70) Ding, Y.; Hay, A. S., *J. Polym. Sci. Polym. Chem.*, **1998**, *36*, 519.

71) Ding, Y.; Hay, A. S., *Macromolecules*, **1996**, *29*, 3090.

72) Ghosal, K.; Chern, R. T., *J. Memb. Sci.*, **1992**, *72*, 91.

73) Robeson, L. M.; Farnham, A. G.; McGrath, J.E., *Polym. Preprints*, **1975**, *16(1)*, 476.

74) Kamps, K. M. P.; Teunis, M.; Wessling, M.; Smolders, C. A., *J. Memb. Sci.*, **1992**, *74*, 193.

75) Imai, Y.; Ueda, M.; Ii, M., *J. Polym. Sci. Polym. Lett. Ed.*, **1979**, *17*, 85.

76) *Polym. Bull.*, **1992**, *29*, 521.

77) Kosan, I., Jap. Pat. 1098629 (1989).

78) Atwood, T. E.; Cinderey, M. B.; Rose, J., B., *Polymer*, **1993**, *34*, 1321.

79) Hergenrother, P. M.; Jensen, B. J.; Havens, S. J., *Polymer*, **1988**, *29*, 358.

80) *J. Polym. Sci.: B : Polym. Phys.*, **1993**, *31*, 1061.

81) *J. Polym. Sci.: A : Polym. Chem.*, **1991**, *29*, 965.

82) Kricheldorf, H. R.; Jahnke, P., *Makromol. Chem.*, **1990**, *191*, 2027.

83) Ding, Y.; Hlil, A.; Hay, A. S., *J. Polym. Sci.: A : Polym. Chem.*, **1998**, *36*, 1201.

84) Meng, Y. Z.; Hay, A. S.; Jian, X. G.; Tjong, S. C., *J. Appl. Polym. Sci.*, **1998**, *68*, 137.

85) Lu, J.; Hlil, A.; Hay, A. S.; Maindron, T.; Dodelet, J. P.; Lam, J.; D'Iorio, M., *J.*

Polym. Sci.: A : Polym. Chem., **2000**, *38*, 2740.

- 86) Lu, J.; Hlil, A.; Meng, Y.; Hay, A. S.; Tao, Y.; D'Iorio, M.; Maindron, T.; Dodelet, R., *J. Polym. Sci.: A : Polym. Chem.*, **2000**, 38, 2887.
- 87) Sapp, S.; Sotzing, G. A.; Reynolds, J. R. *Chem. Mater.* **1998**, 10, 2101.
- 88) Mazur, S.; Lugg, P. S.; Yarnitzky, C. *J. Electrochem. Soc.; Electrochem. Sci. and Techn.* **1987**, 134, 346.
- 89) Krause, L. J.; Bales, J. L. *J. Electrochem. Soc.; Electrochem. Sci. and Techn.* **1988**, 135, 1137.
- 90) Viehbeck, A.; Goldberg, M. J.; Kovac, C. A. *J. Electrochem. Soc.; Electrochem. Sci. and Techn.* **1990**, 137, 1460.

CHAPTER TWO: FUNCTIONAL POLY(ARYL ETHER SULFONE)S CONTAINING TETRAHYDRO[5]HELICENE SUBUNITS

II.1 Introduction

As outlined in the preceding chapter, tailoring of poly(aryl ether) properties may be accomplished through either the introduction of pendent groups or the design of novel monomers which vary structurally from the norm. Of the novel monomers reported in the literature, most lead to unfunctionalizable polymers limiting post polymer grafting or crosslinking. Functional poly(aryl ether)s have been prepared through post polymerization reactions such as replacement of aromatic bromine with nucleophilic amines, direct amination by electrophilic amine and the amination of lithiated polysulfones via azides and other electrophilic synthons.¹ There have been few examples of the preparation of functionalized poly(aryl ether sulfone)s by direct polycondensation (Figure II.1). The direct polycondensation of sulfonated 4-chlorophenylsulfone² and bis(4-fluorophenyl)-3-aminophenylphosphineoxide³ with BPA yielded poly(aryl ether sulfone)s containing either sulfonate or amino groups, respectively. Pendent aldehyde groups have also been incorporated into poly(aryl ether sulfone)s via polycondensation of 4-chlorophenylsulfone and 5,5'-methylene bis-salicylaldehyde.⁴ Also, the nucleophilic polycondensation of a novel dicyanoarylene biphenol monomer with 4-fluorophenylsulfone has been reported.⁵

Figure II.1 Functional poly(aryl ether sulfone)s from direct polycondensation.

The design of a new dihalide monomer suitable for the synthesis of poly(aryl ether sulfone)s needs to meet both variation on structure linearity and the incorporation of an inert functionality available for post polymer transformations. The introduction of anhydride groups is useful as reactive sites along polymer mainchains or at chain ends as they can react with amines, alcohols and epoxides. Anhydride-containing poly(aryl ether sulfone)s may also have additional characteristics such as enhanced adhesion property for potential applications as reactive polymer modifiers, compatibilizers and coupling agents to reduce the interfacial tension between inorganic fillers and the polymer. The direct introduction of anhydride groups into poly(aryl ether sulfone)s is difficult, as nucleophilic polycondensations using anhydride-containing monomers may be troublesome.

Accordingly, the N-phenylimido group, which is chemically inert under polycondensation conditions, can be used as a latent anhydride group and introduced into poly(aryl ether sulfone)s through the nucleophilic polycondensation of an appropriately functionalized bisphenol. The imide group in the polymer has been shown to undergo a facile transimidization at elevated temperatures with hydrazine and amino acids to afford poly(aryl ether sulfone)s containing reactive amine and acid groups (Figure II.2).⁶

Figure II.2 Functionalized poly(arylene ether sulfone)s via transimidization.

The choice of core, 5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic anhydride II-1 (Scheme II.1), has proven to be very versatile in the author's research group. Compound II-1, contains an anhydride group and has been derivatized to an AB-type amino-anhydride monomer and AA-type diamines for the preparation of a series of novel polyimides (Figure II.3).⁷

Figure II.3 Polyimides and poly(aryl ether imide)s derived from core II-1

With proper substitutions on the two terminal phenyl rings of compound II-1, a novel A_2X -type dihalide monomer can be realized, where “X” represents the imide functionality and “A” corresponds to activated fluorine (Figure II.4). Subsequent copolymerization with 4-fluorophenyl sulfone and bisphenol A should lead to structurally modified UdelTM poly(aryl ether sulfone)s.

Figure II.4 Proposed difluoro sulfone monomer

II.2 Monomer Synthesis and Characterization

The synthesis of monomer II-4 was accomplished in three steps from compound II-1 (Scheme II.1). The synthesis of II-1 has been successful on both small and large scale (1 kg) in the laboratory.⁷ The facile chlorosulfonylation of compound II-1 at 5 °C through reaction with chlorosulfonic acid gave the corresponding bischlorosulfonyl derivative, II-2 in a good yield.⁸ The presence of sulfonyl chloride functional groups was

Scheme II.1 Synthesis of tetrahydro[5]helicene based A_2X difluorosulfone II-4.

indicated by IR through the appearance of two stretches at 1375 and 1200 cm^{-1} . The structure of disulfonyl chloride II-2 was confirmed through ^1H NMR (400 MHz), which showed one aromatic singlet and two aromatic doublets, indicating a symmetrical substitution pattern. The 2D ^1H NMR NOESY spectrum indicated a correlation between the aromatic singlet and the ethylene protons, proving the structure to be symmetrically

substituted at the 3- and 12-positions (Figure II.5). The ^{13}C NMR (100 MHz) spectrum also gave further indication to a symmetric substitution, giving rise to nine aromatic carbons, two aliphatic carbons and one carbonyl carbon. The Friedel-Crafts reaction of II-2 and fluorobenzene in the presence of aluminum chloride afforded the difluoro-anhydride II-3.⁹ The symmetric electrophilic substitution of fluorobenzene was confirmed by ^1H NMR (400 MHz) which gave rise to two aromatic protons appearing as the characteristic triplet and quartet and not two doublets due to the spin coupling of ^{19}F (Figure II.6a). The ^{13}C NMR spectrum showed the correct number of carbons along with the expected ^{13}C - ^{19}F couplings. The reactivity of anhydrides as electrophiles in the presence of a Lewis acid is well known, however did not occur in this situation, as confirmed by the presence of anhydride stretches at 1837 and 1769 cm^{-1} in the IR spectrum. The imidization of II-3 with aniline in DMAc in the presence of an azeotropic solvent gave monomer II-4. The IR spectrum shown the characteristic imide stretches at 1764 and 1710 cm^{-1} owing to complete imidization as no anhydride or amic acid stretches were observed. The monomer appeared to be non-crystalline and showed a glass transition at 141 $^{\circ}\text{C}$ by differential scanning calorimetry (DSC). The ^1H NMR spectrum gave rise to phenyl imide proton resonances (Figure II.6b) in addition to the resonances observed from II.3 and the ^{13}C NMR spectrum showed the proper number of magnetically different carbon atoms. The ^{19}F NMR spectrum of II-4 showed a single resonance at -103.73 ppm compared to -104.08 ppm for 4-fluorophenylsulfone, relative to CFCl_3 . The relative reactivities of activated aryl fluoride monomers to nucleophilic displacement reactions has been related to the chemical shift of the respective fluorine

atom. Due to the similar chemical shifts relative to CFCl_3 , the reactivity of monomer II-4 should be very similar to 4,4'-difluorophenylsulfone which should lead to nearly random copolymers.

Figure II.5 2D ^1H NMR NOESY spectrum of II-2.

Figure II.6 ^1H NMR spectra of the aromatic region of (A) II-3 and (B) II-4

II.3 Polymer Synthesis and Characterization

A series of copolymers **II-5a-d** were obtained by the polycondensation of A_2X difluoro monomer **II-4** through the carbonate process. A recently reported process which involves the use of cesium carbonate as base and magnesium hydroxide to aid in the removal of displaced fluoride, was employed for polycondensation.¹¹ A series of copolymers **II-5a-d** and homopolymer **II-5e** were prepared through the polycondensation of **II-4** with 4-fluorophenylsulfone and BPA (Scheme II.2). All polymers were isolated as yellow powders or fibers.

Scheme II.2 Polycondensation of **II-4** with BPA to give **II-5a-e**.

Incorporation of monomer II-4 into poly(aryl ether sulfone)s was confirmed by IR, ^1H NMR and UV\Vis spectroscopic methods. All polymers displayed carbonyl peaks due to the N-phenyl imide at 1770 and 1710 cm^{-1} in their IR spectra, which corresponded exactly to those of monomer II-4. The ^1H NMR spectra of poly(aryl ether sulfone)s 5 showed the presence of the ethylene protons from II-4 at 2.5, 3.0 and 4.2 ppm and the methyl protons from BPA at 1.69 ppm, further indicating the incorporation of II-4. In order to quantify the content of II-4 incorporated into copolymers II-5a-d, UV\Vis spectroscopy was used to construct a Beer-Lambert calibration curve of absorbency versus monomer concentration. From this calibration curve, the mole fraction of monomer II-4 in copolymers II-5a-d was determined to be in a range of 4.9 % to 42 %. A linear relationship between the mole percentage of incorporated II-4 and the measured T_g of copolymers II-5, was found (Figure II.7). The T_g values of poly(aryl ether sulfone)s II-5a-d ranged from 200 °C to 251 °C. It was apparent that the increase in chain rigidity of the resulting polymers, due to the presence of the rigid tetrahydro[5]helicene moiety, had a significant effect on T_g . The higher the content of II-4 in the polymer, the higher the T_g . With a measured T_g of 290 °C, homopolymer II-5e is an anomaly to this linear relationship, which may be reasoned due to the limited molecular weight achieved. However, a higher molecular weight sample of II-5e would have a very high T_g , close to 330 °C as extrapolated from the graph in Figure II.7. Furthermore, the interpolated T_g of 192 °C for the parent polysulfone falls in the range of reported T_g values (184-195 °C).¹²

Figure II.7 T_g vs. mole fraction of monomer II-4 in copolymer II-5a-e.

Gel permeation chromatography (GPC) measurements, relative to polystyrene standards, showed a decrease in molecular weight as the content of II-4 increased in poly(aryl ether sulfone)s. Due to the U-shape molecular structure of II-4, the hydrodynamic volume of the polymers becomes increasingly smaller and subsequently retention times become longer as the II-4 content increases. The measured inherent viscosity values of poly(aryl ether sulfone)s II-5a-e exhibited a similar trend. Poly(aryl ether sulfone) II-5e had a much lower viscosity (0.19 dL/g) than copolymers II-5a-d

(0.64 - 0.33 dL/g). Attributed to the molecular structure of monomer II-4, the apparent molecular weights of all polymers II-5a-e should be lower than the actual values.

Table 1. Characterization of PAESs derived from A₂X difluoride II-4.

Polymer	II-4 in feed ^a (mol %)	II-4 in polymer ^b (mol %)	T _g ^c (°C)	T _d ^d (°C)	M _w ^e	M _n ^e	M _w / M _n	η _{inh} ^f (dL/g)
II-5a	5	4.9	200	500	126000	54000	2.33	0.64
II-5b	20	16	213	436	33800	16900	2.00	0.35
II-5c	35	29	231	469	21700	11400	1.90	0.33
II-5d	50	42	251	408	19300	9900	1.95	0.33
II-5e	100	100	290	433	18800	12600	1.50	0.19

^a Mole fraction of II-4 used in feed.

^b Mole fraction of II-4 incorporated in the polymer as determined from UV/Vis calibration curve.

^c From DSC analysis under nitrogen at a heating rate of 10 °C/min.

^d Onset temperature for 5% weight loss, as assessed by TGA under nitrogen at 10°C/min.

^e Measured by GPC relative to polystyrene standards.

^f Inherent viscosity in CHCl₃ at 25 ± 0.1 °C (0.5 g/dL).

The actual and polystyrene equivalent molecular weights could be compared for end-capped poly(aryl ether sulfone)s. The same copolymerization of II-5b was performed in the presence of 1 mol % excess of 4-fluorophenyl sulfone and 2 mol % of 3,5-di-tertiary-butylphenol relative to BPA (Figure II.8). The resulting end-capped polysulfone, II-5be had a T_g of 212 °C, similar to that of the copolymer II-5b (213 °C), but had a slightly lower inherent viscosity (0.28 dL/g) and a lower molecular weight (M_n

14700) by GPC. From the ^1H NMR spectrum of the end-capped poly(aryl ether sulfone), the actual number-average molecular weight was calculated to be 45 300, using the ratio of the integrals of the methyl peak of BPA and the tert-butyl peak of the end groups. By comparing the viscosity of 0.35 dL/g and an apparent number-average molecular weight of 16 900 for polymer II-5b, all poly(aryl ether sulfone)s containing the U-shape like tetrahydro[5]helicene unit should have much higher molecular weights than their apparent molecular weights determined by GPC.

Figure II.8 End-capped poly(aryl ether sulfone) II-5be.

II.4 Post Polymerization Transformations and Characterization

When the parent poly(aryl ether sulfone) II-5b was subjected to the treatment of ethanolic potassium hydroxide in DMAc at 100 °C, polymer chain degradation occurred within an half hour by GPC analysis. Alternatively, a fine suspension of the II-5b in ethanolic potassium hydroxide at the same temperature showed no degradation over a

long period of time. The testing results imply that transformation of the phenylimido into anhydride group in polysulfone should be done under heterogeneous base hydrolysis conditions (Scheme II.3). Thus, the treatment of II-5b as a fine suspension in ethanolic potassium hydroxide at 70 °C within 30 min led to a complete hydrolysis of the imide group with no apparent polymer degradation as analyzed by GPC.¹³

Scheme II.3 Hydrolysis of imide polymer II-5b to anhydride polymer II-6.

For comparison, the IR spectrum of anhydride polymer II-6 is shown together with those of anhydride II-3 and the precursor imide polymer II-5b (Figure II.9). The disappearance of the carbonyl stretch of the imide functionality at 1767 and 1710 cm^{-1} and the appearance of the characteristic carbonyl stretch of the anhydride moiety at 1837 and 1767 cm^{-1} , indicate clearly the successful transformation of the imide to anhydride functionality. The thermal properties of anhydride containing polysulfone II-6 remained unchanged, having a T_d of 410 °C and a T_g of 210 °C.

Figure II.9 IR spectra (1100 – 1950 cm^{-1}) of (a) anhydride II-3, (b) imide polymer II-5b, and (c) anhydride polymer II-6.

The incorporation of a latent anhydride group into the polysulfone mainchain and subsequent functional group transformation has been successfully demonstrated. Grafting and crosslinking reactions on the anhydride functionality may be achieved through many amino containing molecules to give desired properties for specific applications. In order to demonstrate the accessibility of the anhydride group, a grafting and crosslinking experiment was completed with propargylamine. First a model propargylimide II-7 was prepared, which had a measured exotherm at 311 °C (DSC), representing the thermal reaction (trimerization) of the pendent acetylene group. Subsequent DSC scans showed no further exothermic reaction suggesting complete trimerization. The anhydride containing copolymer of end-capped II-5be was converted

to the corresponding propargylimide **II-8** under the same conditions as for the preparation of the model compound **II-7** and was thermally crosslinked (Scheme II.4).

Scheme II.4 Synthesis of propargyl-imide **II-7** and proposed structure from the thermal trimerization reaction.

The depletion of the crosslinking exotherm was monitored DSC (Figure II.10), where after four heating profiles from 25 °C to 400 °C a crosslinked copolymer was obtained that swelled in conventional solvents and had a slight increase in T_g . This demonstrates the potential use of the anhydride group as a site for grafting and crosslinking reactions leading to desired properties.

Figure II.10 DSC traces of (a) compound II-7 and polymer II-8: first scan (b) and second scan (c) at a heating rate of 10 °C/min under nitrogen.

II.5 Macrocylic Oligomers

The unique U-turn structure of the bridged *o*-terphenyl monomer II-4 led to a very interesting occurrence. During subsequent copolymerizations of II-4 to give a series of copolymers II-5a-e, increasing amounts of a consistent peak in the GPC chromatographs appeared upon increasing content of monomer II-4. As each of the prepared polymers were reverse precipitated in order to obtain high molecular weight polymer, there existed low molecular weight fractions of the polymerizations. The resulting low molecular weight species of II-5b were analyzed by MALDI-TOF Mass Spectroscopy and revealed the presence of macrocylic oligomers (Figure II.11).

Figure II.11 MALDI-TOF MS of macrocyclic oligomers from II-5b.

The presence of only II-MC1, II-MC2 and II-MC3 indicates the potential preference for II-4 to form the smallest possible macrocyclics. Upon comparison of the MALDI-TOF-MS from polymer II-5b (Figure II.11) to the GPC chromatogram (trace (a), Figure II.12), the relative intensities match for the three macrocyclics. This results in a method of monitoring the population of macrocyclics when attempting to exclusively synthesize II-MC1 under high dilution conditions. The one pot synthesis of macrocyclic oligomers in a 1 wt/vol % homopolymerization resulted in the collection of increased amounts of II-

MC1 and no II-MC3 (trace (b), Figure II.12). An attempt was made to prepare II-MC1 through a sequential addition homopolymerization. The polymerization pot containing the phenoxide salt of BPA was initially prepared followed by the slow addition of a DMAc solution of II-4 over 10 hours through the use of a syringe pump at polymerization temperature. The resulting macrocyclics showed the almost exclusive preparation of II-MC1 with only small amounts of II-MC2 (trace (c), Figure II.12).

Figure II.12 GPC of (a) macrocyclic oligomers from II-5b, (b) 1 wt/vol % one pot homopolymerization and (c) 1 wt/vol % sequential homopolymerization.

II.6 Structure-Property Relationships from Tetrahydro[5]helicene Incorporation

The incorporation of the tetrahydro[5]helicene subunit into poly(aryl ether sulfone)s allowed for the determination of structure-property relationships through the observed trends in a series of copolymers based on UdelTM. The first corresponds to the measured T_g 's of the series of copolymers, indicating a direct correlation between increasing mole percent incorporation and the measured T_g . An indication of the overall structure of the poly(aryl ether sulfone)s was assessed through a comparison of the apparent molecular weight as measured by GPC to that obtained via ¹H NMR of the corresponding end-capped copolymer. The calculated molecular weight of the end-capped polymer was greater compared to the value obtained by GPC, owing to the U-shape of the tetrahydro[5]helicene subunit and an overall decrease in linearity as GPC retention times are calibrated using linear polystyrene standards.

With respect to the solubility of the copolymers, there appeared to be no adverse effect to tetrahydro[5]helicene, as all polymers were soluble in chloroform and methylene chloride. However, the mechanical properties appeared to have decreased through the qualitative assessment of film toughness. Relatively strong films were obtained up to 20 % incorporation ratios of the tetrahydro[5]helicene subunit, otherwise brittle films resulted.

As a result of the inherent structure of the monomer, macrocyclic formation was observed with relative ease and monocyclic oligomers were obtained almost exclusively. In comparison to reported macrocyclic oligomers, as outlined in the previous chapter, monocyclics appeared unattainable as the oligomers ranging from $n = 2$ to 6-10 resulted

dependent on the structure of the monomers. When linear para-substituted monomers were used macrocyclics from $n = 2$ -10 were reported, in comparison to ortho-phenyl substituted monomers which afforded macrocyclics from $n = 2$ -6.

II.7 Conclusions

The design and synthesis of a novel A_2X monomer, N-phenyl 3,12-di(4-fluorobenzenesulfonyl)-5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic imide **II-4**, allowed for the correlation of structure dependence on the resulting properties of a series of poly(aryl ether sulfone)s. The gradual increase of the content (up to 42 mol%) of the rigid tetrahydro[5]helicene unit incorporated into a polysulfone, derived from 4-fluorophenylsulfone and bisphenol A, resulted in a linear increase in the glass transition temperature, ranging from 200 °C to 251 °C. The post polymerization chemical transformation of the N-phenylimido group into the corresponding anhydride was achieved under heterogeneous base hydrolysis conditions. The anhydride containing polysulfone can be converted to the corresponding propargylimide and thermally crosslinked at 315 °C and swelled in conventional solvents. This demonstrates that through the use of an rigid helical A_2X monomer the glass transition temperature can be increased while concurrently controlling the solubility before and after crosslinking.

The very interesting phenomenon of macrocyclic formation occurred due to the U-turn nature of the *o*-terphenyl helical unit. The percentages of cyclic oligomers formed was controllable, with high percentages of the monocyclic oligomer.

The questions arising from this work were twofold: (1) were the increases in T_g a result of the rigid helical structure or the inherent *o*-terphenyl structure? and (2) how would the macrocyclic phenomenon occur in an analogous polymer allowing for more rotation about the central core?

II.8 Experimental Section

Materials

Compound II-1 was prepared from α -tetralone according to the previously reported method.⁷ 4,4'-(isopropylidene)diphenol (BPA) was purchased from the Aldrich Chemical Company, recrystallized from toluene prior to polymerization. Bis-(4-fluoro)phenylsulfone was purchased from Marshallton and used as received.

All other reagents chlorosulfonic acid, nitrobenzene, fluorobenzene, anhydrous aluminum chloride, aniline, chlorobenzene, 3,5-ditert-butylphenol, propargylamine, dimethylacetamide, cesium carbonate and magnesium hydroxide were purchased from Aldrich Chemical Company and used as received.

All deuterated solvents were purchased from Canadian Isotopes Incorporated and used as received.

Measurements

¹H and ¹³C NMR spectra were recorded on a Bruker-400 instrument using tetramethylsilane as an internal reference. ¹⁹F NMR spectra were recorded on a Varian XL-300 using trifluoroacetic acid as an external reference. Infrared measurements were performed on a Bomen Michelson 120 FTIR spectrometer. Low (EI) and high resolution mass spectra were obtained on VG 7070E and Kratos Concept IIIH spectrometers, respectively. UV-Vis absorption spectra were measured on a Varian Cary 3 spectrophotometer. Melting points were obtained with a Fisher-Johns apparatus and are uncorrected. Gel permeation chromatography (GPC) was performed using chloroform at

ambient temperature and a flow rate of 1.0 mL per min. Weight average and number average molecular weights were calculated relative to polystyrene standards. A UV detector set at 254 nm was used for detection. Inherent viscosities were measured in chloroform solution at $25 \pm 0.1^\circ\text{C}$ using an Ubbelohde dilution viscometer. Glass transition temperatures were determined on a Seiko 220C DSC at a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen flow (50 mL/min). Thermal stabilities of the polymer samples were determined using a Seiko 120 TG/DTA analyzer run from 25°C to 800°C at a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen flow (100 mL/min). MALDI-TOF mass spectra were obtained on a Kratos Kompact MALDI 3 time-of-flight mass spectrometer, using a dithranol/lithium bromide (20:1 by weight) matrix.

Monomer Synthesis

Synthesis of disulfonylchloride anhydride II-2.

In a 250 mL 2-necked round-bottomed flask equipped with a magnetic stir bar and nitrogen inlet/outlet was dissolved anhydride II-1 (0.500 g, 0.014 mol) in dichloromethane (120 mL). The solution was cooled to 0 °C in an ice-NaCl bath, chlorosulfonic acid (7.6 mL, 0.144 mol) was added dropwise with vigorous stirring, maintaining the reaction temperature below 5 °C. The solution became deep yellow-brown in color and was stirred at room temperature overnight. The reaction mixture was then added slowly to ice water (350 mL) with vigorous stirring. The two phases were partitioned. The aqueous phase was extracted with dichloromethane (100 mL). The combined organic phases were washed with water (50 mL) and dried over anhydrous magnesium sulfate, filtered and rotary evaporated. After drying under high vacuum at room temperature, II-2 was obtained as a yellow amorphous powder: 6.48 g (83%, crude). The crude product II-2 was dissolved in dichloromethane (400 mL), then concentrated to a half of its volume. Acetonitrile was then added (80 mL) and the solution was concentrated until cloudiness appeared and was left to stand. The purified product II-2 was collected as a yellow amorphous powder: 3.15 g (40 %); ^1H NMR: (400 MHz, DMSO- d_6) 8.08 (s, 1H), 7.66 (d, 1H), 7.27 (d, 1H), 4.10 (d, 1H), 3.15 (m, 2H),

2.70 (m, 1H); ^{13}C (100 MHz, DMSO - d_6) 162.8, 147.9, 139.5, 139.4, 138.6, 132.7, 129.2, 125.7, 125.2, 123.0, 27.3, 23.8; IR (KBr) 1836, 1769, 1375, 1174 cm^{-1} ; MS (EI, m/e, rel. %) 548 (M^+ , 10.9).

Synthesis of difluorosulfone-anhydride II-3.

In a flame dried 250 mL, 3-necked flask equipped with a condenser, nitrogen inlet/outlet and magnetic stirrer, was dissolved the disulfonyl chloride **II-2** (12.0 g, 21.9 mmol) in nitrobenzene (65 mL) upon heating. To the above cooled red solution were added anhydrous AlCl_3 (14.5 g, 109 mmol) and fluorobenzene (42.0 g, 438 mmol), resulting in a dark purplish/black mixture. The mixture was heated to 135 $^{\circ}\text{C}$ for 3.5 h. The solution was cooled to room temperature and then added to an aqueous HCl solution (10 % v/v, 250 mL). After stirring vigorously for 18 h, the layers were partitioned and the aqueous layer was extracted once with methylene chloride (25 mL). The organic phases were combined and concentrated to give a solution containing the product and nitrobenzene. The product was precipitated into aqueous methanol (90 %, 1 L). The solid was collected on a sintered glass filter funnel, dissolved in acetone and again precipitated into aqueous methanol (90 %) to remove any residual nitrobenzene. The pale

yellow solid **II-3** was collected and used without further purification: 9.2 g (63 %); T_m 303 °C (DSC); ^1H NMR (400 MHz, CDCl_3) 8.00 (q, 2H), 7.90 (s, 1H), 7.47 (d, 1H), 7.24 (t, 2H), 7.16 (d, 1H), 4.00 (d, 2H), 2.90-3.10 (M, 4H), 2.55 (M, 2H); ^{13}C NMR (100 MHz, CDCl_3) 166.98, 164.43, 162.34, 141.87, 140.89, 140.54, 139.68, 137.07, 137.02, 136.99, 131.02, 130.78, 130.69, 127.31, 126.87, 125.25, 116.96, 116.74, 28.08, 23.89; ^{19}F NMR (300 MHz, CDCl_3) 27.30 (relative to trifluoroacetic acid); IR (KBr) 1837 and 1769 cm^{-1} (C=O, anhydride); MS (FAB, m/e , relative intensity %) 669 ($\text{M}+\text{H}^+$, 32.4)

Synthesis of difluorosulfone-phenyl imide monomer **II-4**.

In a 50 mL, 2-necked, round-bottomed flask fitted with a nitrogen inlet/outlet and a Dean-Stark trap, was dissolved anhydride **II-3** (4.0 g, 6.0 mmol) in DMAc (25 mL) and chlorobenzene (10 mL) under nitrogen. Aniline (0.8 mL, 9.0 mmol) was then added. The solution was stirred at room temperature for 30 min and heated to reflux overnight. More chlorobenzene was added (30 mL) to azeotropically distill off water. The reaction solution was poured into acidic ethanol (5ml HCl/100 mL). The resulting solids were dissolved in chloroform (10 mL), passed through a short column packed with silica gel (10 g), and eluted with chloroform (100 mL). After removal of chloroform and drying at

70 °C under vacuum (5 mmHg) for 24 h, monomer **II-4** was obtained as a beige colored amorphous powder: 3.3 g (74 %); T_g 141 °C (DSC); ^1H NMR (400 MHz, CDCl_3) 8.00 (q, 4H), 7.89 (s, 2H), 7.53-7.38 (m, 7H), 7.26-7.16 (m, 6H), 4.20 (d, 2H), 2.90-3.10 (m, 4H), 2.55 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) 167.10, 166.94, 164.39, 141.18, 140.64, 139.37, 138.19, 137.74, 137.14, 131.46, 131.04, 130.77, 130.67, 129.16, 128.31, 127.19, 127.12, 126.72, 125.10, 116.94, 116.72, 28.47, 23.71; ^{19}F NMR (300 MHz, CDCl_3) 27.58 (relative to trifluoroacetic acid); IR (KBr) 1764 and 1710 ($\text{C}=\text{O}$, imide) cm^{-1} ; MS (FAB, m/e , relative intensity %) 744 ($\text{M}+\text{H}^+$, 100.0)

Polymer Synthesis

A typical polycondensation procedure for the synthesis of polymers **II-5a** – **II-5e** is given as follows.

In a 25 mL, 2-necked round-bottomed flask, equipped with a magnetic stirrer, nitrogen inlet/outlet, condenser and Dean & Stark trap, was placed BPA (0.4566 g, 2.000 mmol), 4-fluorophenyl sulfone (0.4068 g, 1.600 mmol), monomer **II-4** (0.2975 g, 0.400 mmol), Cs_2CO_3 (0.3421 g, 1.050 mmol) and $\text{Mg}(\text{OH})_2$ (0.0787 g, 1.350 mmol). The mixture was dissolved in DMAc (4 mL, 30 % w/v) and an equal amount of toluene was added. The reaction flask was evacuated with nitrogen for 30 minutes, at which time the mixture was heated to 130 °C (oil bath temperature) for 1 hour and 30 minutes to remove water through azeotropic distillation. The reaction temperature was increased to 165 °C. The solution turned a dark purple color and polymerization was continued until GPC showed no increase in molecular weight and high polymer was obtained by precipitating

into methanol. The filtered polymer was dissolved in chloroform and filtered through Celite to remove inorganic salts. The low molecular weight material was removed via reverse precipitation. All polymers were dried at 100 °C under high vacuum (5 mm Hg) for 24 hours.

End-capped Poly(aryl ether sulfone) II-5be. A 25 mL, 2-necked round-bottomed flask was set up as usual. BPA (0.4566 g, 2.000 mmol), 4-fluorophenyl sulfone (0.4119 g, 1.620 mmol), monomer II-4 (0.2975 g, 0.400 mmol), 3,5-di-tert-butylphenol (0.0082 g, 0.040 mmol), Cs₂CO₃ (0.3421 g, 1.050 mmol) and Mg(OH)₂ (0.0787 g, 1.350 mmol) were dissolved in DMAc (4 mL, 30 % w/v) and 4 mL of toluene was added. The polymerization was carried out in the exact manner as previously outlined.

Post Polymerization Hydrolysis. A chloroform solution of II-5b (150 mg/10 mL) was precipitated into ethanolic potassium hydroxide solution (1 pellet/35 mL) resulting in a finely divided suspension. The suspension was heated to 70 °C and maintained at that temperature for 30 minutes. The suspension was cooled to ambient temperature and acidified with HCl. The polymer was filtered dissolved in CHCl₃, filtered through sintered glass to remove inorganic salts and precipitated into ethanol. The resulting polymer showed approximately 80 % conversion of the phenyl-imide to anhydride. The resulting polymer was hydrolyzed again in the exact manner, collected and dried at 150 °C under high vacuum for 24 hours.

II.7 References

- 1) Guiver, M. D.; Robertson, G. P.; Foley, S., *Macromolecules*, **1995**, *28*, 7612.
- 2) Pak, S. J.; Lyle, S. D.; Mercier, R.; McGrath, J. E., *Polym. Bull.* **1992**, *29*, 477.
- 3) Ueda, M.; Toyota, H.; Ouchi, T.; Sugiyama, J. I.; Yonetake, K.; Masuko, T.; Teramoto, T., *J. Polym. Sci. Part A: Polym. Chem.* **1993**, *31*, 853.
- 4) V. Cozan, E. Butuc, A. Stoleriu and A. Cascaval., *J. Macromol. Sci., Pure Appl. Chem.* **1995**, *A32(5)*, 1067.
- 5) Yang, Haizin, Elke, Edmund and Hay, Allan S., *J. Macromol. Sci., Pure Appl. Chem.* **1995**, *A32(6)*, 1103.
- 6) Herbert, C. G.; Hay, A. S., *J. Polym. Sci. Part A: Polym. Chem.* **1997**, *35*, 1095.
- 7) (a) Wang, Z. Y.; Qi, Y.; Bender, T. P.; Gao, J. P., *Macromolecules*, **1997**, *30*, 764 (b) Bender, T. P.; Qi, Y.; Gao, J. P.; Wang, Z. Y., *Macromolecules*, **1997**, *30*, 6001.
- 8) Wang, Z. Y.; Gao, J. P.; Bender, T. P.; Qi, Y.; MacKinnon, S. M.; Kuang, L.; Chen, J. P.; Meng, X. S., *Polym. Preprints*, **1997**, *38(1)*, 153.
- 9) Martinez, C. A.; Hay, A. S., *J. Polym. Sci. Polym. Chem.* **1997**, *35*, 2015.
- 10) Cotter, R. J. *Engineering Plastics: Handbook of Polyaryl Ethers*. Gordon and Breach Publishers, USA. 1995.

CHAPTER THREE: FUNCTIONAL POLY(ARYL ETHER SULFONE)S CONTAINING *o*-TERPHENYL SUBUNITS

III.1 Introduction

The previous chapter reported the preparation of a series of copoly(aryl ether sulfone)s derived from difluorosulfone monomer II-4.¹ It was shown that increasing mole percentages of II-4 into poly(ether sulfone)s, derived of 4-fluorophenylsulfone and BPA, resulted in a direct linear increase in the measured T_g . However, as the changes in glass transition were attributed to the presence of II-4 within the poly(aryl ether sulfone), it was not obvious whether the changes were a result of the entire structure of II-4 or its inherent *o*-terphenyl subunit. In order to probe the effect of the *o*-terphenyl moiety, a non-bridged *o*-terphenyl III-3, analogous to II-4 was designed for incorporation into poly(aryl ether sulfone)s (Figure III.1).

Figure III.1 Non-bridged *o*-terphenyl monomer III-3 analogous to II-4.

The A₂X *o*-terphenyl difluorosulfone monomer III-3 was designed to be analogous to II-4 containing a masked anhydride functionality. In this case, a labile imide was chosen as a reactive functional group, as it is known to undergo facile transimidization.²⁻⁷

III.2 Monomer Synthesis and Characterization

The specific synthesis of 3,6-dimethyl-4,5-diphenylphthalic anhydride has not been reported explicitly, although a vague reference to its melting point was made.⁸ However, the synthesis of its precursor compounds were reported separately. Condensation of benzil and 3-pentanone in the presence of aqueous potassium hydroxide gives α,β -dimethylanhydracetonebenzil in reasonable yield.⁹ Complete dehydration to 2,5-dimethyl-3,4-diphenylcyclopentadienone (which exists as a white crystalline dimer at room temperature) was achieved using acetic anhydride and sulfuric acid, giving long rectangular prisms upon crystalization.¹⁰ This dimer has been reported to dissociate to its monomer upon heating, to give deep red solutions.¹¹ Therefore, the sequential Diels-Alder reaction with maleic anhydride and subsequent treatment with elemental bromine in bromobenzene, gives 3,6-dimethyl-4,5-diphenylphthalic anhydride III-1, in good yield (Figure III.2).⁸

Figure III.2 Reported synthesis of III-1

The direct sulfonylation of 3,6-dimethyl-4,5-diphenylphthalic anhydride III-1 with 4-fluorobenzenesulfonyl chloride was not possible as the anhydride group of III-1 was not stable to standard Friedel-Crafts conditions. Therefore, the anhydride was blocked by imidization with 2-aminopyridine, to give the resulting imide III-2. The pyridyl imide moiety was found to be stable to both etherification and sulfonylation conditions. However, it is known to be labile when in the presence of more basic amines towards a transimidization reaction.²⁻⁷ The sulfonylation of III-2 with 4-fluorobenzenesulfonyl chloride in the presence of AlCl_3 in nitrobenzene gave monomer III-3 in good yield after flash chromatography (Scheme III.1).

Scheme III-1 Synthesis of monomer III-3 (i) 2-aminopyridine, 1,2-dichlorobenzene, reflux. (ii) 4-fluorobenzenesulfonyl chloride, AlCl_3 , nitrobenzene, 115 °C.

The substitution at the 4'- and 4''-positions was confirmed using ^1H NMR spectrum of **III-3**, which showed two sets of doublets at 6.97 and 7.63 ppm, representing the two aromatic protons on carbons 2' and 3' of the *o*-terphenyl subunit. Additional aromatic resonances were observed for the protons on the 2-pyridyl and fluorophenyl sulfone moieties (Figure III.3). Furthermore, the ^{13}C NMR spectrum of **III-3** exhibited resonances for 17 nonequivalent carbon atoms as expected. The ^{19}F NMR spectrum of **III-3** also showed a single resonance at -103.57 ppm (-27.42 relative to trifluoroacetic acid) for **III-3**, which compares to -103.73 for **II-4** and -104.08 for 4-fluorophenylsulfone (all relative to CFCl_3). It is known that relative reactivities of activated aryl fluoride monomers to nucleophilic displacement polymerization can be related to the ^{19}F chemical shift of the fluorine atom.¹² This suggests that the reactivity of **III-3** compared to 4-fluorophenylsulfone is approximately the same and should lead to random copolymers.

There is a distinct change in the UV/Vis absorption spectra of **III-3** and **II-4** (Figure III.4). For example, there is a hypsochromic shift (blue shift) in λ_{max} of the long wavelength absorption of monomer **III-3** to 323 nm and a decrease in the molar absorptivity to $7740 \text{ Lmol}^{-1} \text{ cm}^{-1}$. This compares to a λ_{max} of 369 nm and a molar absorptivity of $15470 \text{ Lmol}^{-1} \text{ cm}^{-1}$ for the long wavelength absorption of monomer **II-4**, indicating a decrease in the degree of conjugation within the *o*-terphenyl moiety comparing monomer **II-4** to monomer **III-3**.

Figure III.3 ^1H NMR spectrum of III-3 (A) full spectrum, (B) aromatic region

Figure III.4. UV/Vis absorption spectra of monomers III-3 and II-4.

Further support was found upon analysis of energy minimized molecular models of both monomers II-4 and III-3, calculated using a commercial molecular modeling software package. The calculated torsional angle between the phenyl groups of the *o*-terphenyl moieties of III-3 was 51 ° compared to 25 ° for II-4 (Figure III.5). The difference in torsional angle is consistent with the measured UV/Vis absorption spectra.

Figure III.5 MM⁺ optimized molecular conformation of III-3 (left) and II-4 (right).

III.3 Polymer Synthesis and Characterization.

A series of copolymers III-4a-e were obtained by polycondensation of monomer III-3, 4,4'-difluorophenylsulfone and BPA in the presence cesium carbonate and magnesium hydroxide ¹³ in DMAc (Scheme III.2). Copolymers III-4a-c were made from 5, 10 and 20% of monomer III-3, respectively. When polymerizations were attempted with 30 % or higher of monomer III-3, an insoluble polymer gel was formed. All polymers were purified by reverse precipitation and characterized through conventional methods (Table III.1).

Scheme III.2 Synthesis of *o*-terphenyl containing poly(aryl ether sulfone)s.

The molar percent (mol%) incorporation of monomer III-3 in copoly(ether sulfone)s III-4a-c were determined using UV/Vis spectroscopy. It was found that the mol% incorporation ratio of III-3 was, in all cases, lower than the corresponding feed ratios. In an attempt to circumvent this problem, two other polymerization procedures were attempted. Sequential addition polymerization III-4d was started by reaction of monomer III-3 with the total required amount of BPA under normal polymerization conditions. After 2 h, TLC showed the absence of monomer III-3 and GPC analysis showed the formation of desired oligomers, 4-fluorophenyl sulfone was then added to the polymerization reaction. The resulting mol% incorporation ratio for the final polymer was increased slightly from 15% for III-4c to 16.8 % for III-4d. In addition to sequential polymerization, the stoichiometric ratio of BPA monomer to difluoride monomers was

offset to have a small excess of monomer III-3 present within the polymerization reaction. Although the resulting polymer III-4e had a lower molecular weight compared to III-4c-d, its mol% incorporation ratio of III-3 was greatly enhanced.

Table III.1 Characterization of PAES III-4a-e derived from III-3

Polymer	III-3 Feed ^a (mol %)	III-3 incorporated ^b (mol %)	T _g (°C) ^c	T _d (°C) ^d	M _w ^e	M _n ^e	M _w /M _n	η _{inh} ^f (dL/g)
III-4a ^g	5	4.0	193	484	36500	15900	2.30	0.38
III-4b ^g	10	9.7	204	453	19300	10000	1.90	0.22
III-4c ^g	20	15	208	463	46300	22800	2.05	0.38
III-4d ^h	20	16.8	209	467	40300	13900	2.90	0.33
III-4e ⁱ	20	21	201	465	16900	8700	1.90	0.21

^a mol% ratio of III-3 in monomer feed.

^b mol% ratio of III-3 incorporated into polymers III-4a-e determined by UV/Vis spectroscopy.

^c DSC analysis under N₂ at a heating rate of 10°C/min.

^d Temperature for 5% weight loss, as assessed by TGA under N₂ at a heating rate of 10°C/min.

^e Measured by GPC relative to polystyrene standards.

^f Inherent viscosity in CHCl₃ at 25 ± 0.1 °C (0.5 g/dL)

^g Typical polymerization method.

^h Sequential addition copolymerization.

ⁱ Stoichiometric offset copolymerization.

The measured T_g for copoly(aryl ether sulfone)s III-4a-e varied over a 20 °C range, dependent on the mol% incorporation of monomer III-3. As the linear dependency of the measured T_g has been previously observed for copoly(ether sulfone)s

derived from monomer II-4 (Figure III.6),¹ the increase is also linear in the case of polymers III-4a-e.

Figure III.6 T_g versus mole % incorporation from poly(ether sulfone)s III-4a-e derived from III-3 (circles) and poly(ether sulfone)s derived from II-4 (triangles). Dotted lines indicate the T_g range of the parent poly(ether sulfone) derived from BPA and 4-fluorophenyl sulfone.

III.4 Post Polymerization Reaction – Transimidization.

The pyridyl imide is known to undergo a transimidization reaction at elevated temperatures in the presence of an amine of increased basicity compared to the 2-aminopyridine.²⁻⁷ In order to determine if the 2-aminopyridyl imide was prone to transimidization a model reaction was investigated. The transimidization of **III-2** was attempted with propargylamine, an alkyl amine which is also susceptible to ring forming reactions at temperatures in excess of 300 °C as shown in the previous chapter (Scheme III.3).

Scheme III.3 Model synthesis of **III-5** via transimidization.

The resulting propargyl imide **III-5** was fully characterized using conventional techniques. The shift of imide stretches in the IR spectrum from 1770 and 1711 cm^{-1} in **III-2** to 1764 and 1708 cm^{-1} for **III-5** was the first indication of transimidization. The ^1H NMR of **III-5** showed the disappearance of all resonances corresponding to the substituted pyridyl group and the appearance of a resonance at 4.4 ppm corresponding to the methylene protons of the propargyl imide (Figure III.7).

Transimidization of poly(ether sulfone) **III-4d** with propargylamine under the same conditions for the preparation of the model **III-5** compound, gave poly(aryl ether sulfone) **III-6** having a reactive acetylene group. The presence of propargyl imide was initially characterized by ^1H NMR, which showed the appearance of the same resonance corresponding to the methylene protons of the propargylimide (Figure III.8).

Figure III.7 ^1H NMR of **III-5** from transimidization.

Figure III.8 ^1H NMR of **III-6** from post polymer transimidization of **III-4c**.

Poly(ether sulfone) **III-6** also showed a decreased glass transition temperature of 184 °C as compared to the precursor polymer **III-4d** which had a T_g of 209 °C. The thermal reactivity of the acetylene group was demonstrated in the previous chapter with the thermal crosslinking of **II-8**. The DSC was used to monitor the course of the crosslinking reaction, which showed an exotherm at approximately 360 °C in the first run and an increased T_g of 212 °C in the second run (Figure III.9). Furthermore, the crosslinked poly(aryl ether sulfone) **III-6** only swelled but did not dissolve in conventional solvents.

Figure III.9 DSC traces of poly(ether sulfone) III-6: (a) pre-thermal treatment. (b) post-thermal treatment.

III.5 Macrocyclic Oligomers.

The polymer growth was observed with increasing reaction time, as monitored by GPC. However, the amount of low molecular weight materials also increased as polymerization continued (Figure III.10). The observation implies that the polymer grows in molecular weight while producing small molecules or an oligomer. As expected GPC analysis showed an initial increase in the molecular weight of the polymer and a simultaneous decrease in the amount of low molecular weight species, after 2 h and 4 h of polymerization. However, on examination of the polymerization reaction after 12 h there was a further increase in the apparent molecular weight of the polymer and a large increase in the amount of low molecular weight materials formed. The low molecular

weight materials appeared to contain monomer **III-3** in a higher abundance, as confirmed by GPC analyses at two different wavelengths (254 nm and 325 nm in Figure III.10c and III.10d). After reverse precipitation, the mol% incorporation ratio of **III-3** in the low molecular weight fraction was calculated to be 57%.

Figure III.10 GPC traces of copolymerization **III-4d**: (a) 2 h @ 254 nm. (b) 4 h @ 254 nm. (c) 12 h @ 254 nm. (d) 12 h @ 325 nm.

Additionally, low molecular weight fractions of selected polymers (**III-4c** and **III-4d**) were analyzed by MALDI-TOF MS spectroscopy. Each was shown to contain macrocyclic that contained a minimum of one *o*-terphenyl unit. These samples were designated **III-Cyc4c** and **III-Cyc4d** respectively. The distribution of macrocyclic materials was effected by the method of polymerization. As shown by the relative peak

intensities for each macrocyclic measured by MALDI-TOF MS, III-Cyc4c on average contained lower molecular weight macrocycles than III-Cyc4d (Table III.2). The difference must be due to the polymerization method that yielded each sample. As macrocyclics III-Cyc4c and III-Cyc4d were isolated from standard and sequential polymerization reactions respectively, the sequential polymerization selectively produce higher molecular weight macrocycles than standard polymerization conditions.

Table III.2 MALDI-TOF MS analysis of III-Cyc4c and III-Cyc4d.

<p style="text-align: center;">III-Cyc4c, III-Cyc4d</p>						
Macrocyclic	Ratio of a:b:c			Mw calc. (amu)	Relative intensity	
	a	b	c		III-Cyc4c ^a	III-Cyc4d ^a
III-M ₁	1	1	0	909	0.25	0.11
III-M ₂	1	2	1	1351	1.00	1.00
III-M ₃	1	3	2	1794	0.58	0.74
III-M ₄	1	4	3	2234	0.23	0.13
III-M ₅	2	4	2	2702	0.10	0.05
III-M ₆	2	5	3	3144	0.03	0.02

^a % Intensity as observed in the MALDI-TOF mass spectrum.

Coupling the MALDI-TOF spectra with the observations made using GPC, the progressive formation of cyclic macromolecules over the course of the polymerization indicates that polymers containing monomer **III-3** have a tendency to cyclodepolymerize. This behavior is not observed for polymers derived from monomer **II-4**. Monomer **III-3** has a higher degree of molecular rotation as compared to monomer **II-4**, owing to its non-bridged *o*-terphenyl moiety, which allows the reactive chain ends to attack the growing backbone or to cyclodepolymerize via a transesterification reaction (Figure III.11).

Figure III.11 Potential route of cyclodepolymerization

III.6 Potential Application

Poly(aryl ether)s have been used in the electronics environment as insulators for many years, owing to high temperature performance and hydrolytic stability. The investigation of novel potential application evolves directly from the functionalization tailored into the polymer. The ability of poly(aryl ether sulfone)s derived from **III-3** to undergo facile transimidization with a nucleophilic alkyl amine lends itself to the development of methods to potentially enhance existing applications or be further developed in the realization of new applications. With the onset of organic films and modifications of surfaces, the objective was to demonstrate that poly(aryl ether)s derived from **III-3** allowed for surface modification. Surface modifications were attempted using either a step-wise or a one pot method, utilizing 3-aminopropyltriethoxysilane (APTES) as the linking moiety. The alkyl amine has similar nucleophilicity to both hexylamine and propargylamine previously demonstrated to facilitate transimidization of 2-pyridyl phthalimides. The surfaces will be characterized using cyclic voltammetry and scanning electron microscopy.

III.6.1 Methods of Surface Modification

The surfaces were modified by either a step-wise (**III-SSW**) or a one pot method (**III-SOP**) (Figure III.12). The step-wise method involved the initial treatment of indium-tin-oxide (ITO) coated glass, a transparent conducting glass, with 3-aminopropyltriethoxysilane. The interaction of triethoxysilane groups with the free hydroxy groups on the ITO surface, has been known to form self assembled

monolayers.¹⁴ The aminated surface was then dip coated five times in a chloroform solution of polymer III-4d (100 mg/20 ml) and cured at 230 °C for 2 hrs. The alternative method of modification, the one pot method, was done by suspending two cleaned ITO surfaces in a DMAc solution of polymer III-4d (50 mg), APTES (10 mg) and heated to 110 °C overnight under a nitrogen atmosphere. Both modified surfaces III-SSW and III-SOP were sonicated (1 hr) in DMAc before characterization.

Figure III.12 Methods for the surface modification of ITO glass with polymer III-4d

III.6.2 Surface Characterization

The modified surfaces, III-SSW and III-SOP were characterized using both cyclic voltammetry and scanning electron microscopy. Cyclic voltammetry allowed for comparisons of insulating ability to be made on a qualitative basis through measuring the

current passing through the modified surface. The standard ferrocene couple was measured using a bare ITO glass slide as the working electrode, platinum wire as the counter electrode, a silver wire as the pseudo reference and a 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile as the electrolyte (Figure III.13). The measured ferrocene couple had a half wave potential of 0.35 V and a $\Delta E = 0.03$ V (difference between reduction and oxidation).

Figure III.13 Cyclic voltammogram ferrocene

In order to determine the relative insulating abilities of the modified surfaces, the bare ITO working electrode was replaced with III-SSW followed by III-SOP. The subsequent cyclic voltammogram of III-SSW (Figure III.14) indicated the surface was completely insulating over the range of -1.5 V to 3.0 V. The analysis of the cyclic voltammogram of III-SOP showed that the surface was still conductive, however

increased voltages were required for oxidation and reduction as observed by the same half wave potential of 0.36 V and a $\Delta E = 0.36$ V.

Figure III.14 Cyclic voltammograms of modified ITO surfaces as working electrodes

The second method of characterization used was scanning electron microscopy leading to pictures of the surface and a relative measure of both insulating and surface topography. The working electrodes III-SSW and III-SOP were cut into small sections ($\sim 1 \text{ cm}^2$) and mounted using carbon tape, onto an aluminum slide suitable for measurement. Each of the two aluminum slides contained a bare ITO sample, a III-SSW sample and a III-SOP sample. One of the slides was sputter-coated with gold and the other was untouched. SEM analysis of the virgin surfaces showed the same relative insulating pattern compared to the cyclic voltammetry results. Under the same brightness and contrast, images were obtained and the relative brightness is an indication to how effective the insulator (Figure III.15). When conducting surfaces are investigated, images

show a great deal of brightness (appearing white) as a result of the enhanced ability of the surface to emit secondary electrons and have induced surface conductivity.¹⁵

Figure III.15 SEM images under the same brightness and contrast conditions of virgin samples: bare ITO (left), III-SOP (center) and III-SSW (right).

Investigating the surface topology allowed for the characterization of differences of the surfaces as a result of the modification method (Figure III.16). The comparison of unmodified ITO to III-SOP showed the two to have very similar topologies, as both are relatively featureless at the 1 μm level of magnification. However, III-SSW shows a large amount of surface topology as indicated by numerous high points appearing as white dots.

Figure III.16 SEM images under the same brightness and contrast conditions of gold coated samples: ITO (left), III-SOP (center) and III-SSW (right).

The topology can be discussed in light of the method of modification. The dip-coating method led to a film of increased thickness relative to the one-pot method, due to more polymer being present as a result of evaporation of solvent. The thermal treatment, above the glass transition temperature of polymer III-4d, may have allowed for the reorganization of the film and increases the degree of entanglement of unanchored polymer. Conversely, the one pot method kept the polymer in solution throughout the experiment, leading to fewer amounts of polymer chains becoming entangled in the film.

In summary, the facile transimidization reaction has allowed for the surface modification of hydroxylated surfaces. In the areas of electronic packaging, the adhesion of high temperature thermoplastics as transparent protective coatings has potential. In general, the application of these materials is limited due to the bulk of commercially available coatings, however it demonstrates that poly(aryl ether sulfone)s can be designed for function.

III.7 Structure-Property Relations from *o*-Terphenyl Incorporation

The properties resulting from the incorporation of tetrahydro[5]helicene subunits into poly(aryl ether sulfone)s were outlined in Chapter One. The resulting concerns to the effect of *o*-terphenyl containing poly(aryl ether sulfone)s included; to what extent the increases in T_g could be attributed to the *o*-terphenyl structure and how would the increased rotational freedom effect macrocyclic formation.

Comparing the synthetic strategies of II-4 and III-3, the stability of the anhydrides II-1 and III-1 were not the same, as the anhydride III-1 was reactive in the presence of the Lewis acid. The loss of anhydride stability in III-1 may be attributed to the decrease in conjugation resulting from the increased free rotation about the central phenyl ring. Therefore, initial formation of the imide was required in order to protect the anhydride from acting as an electrophile in the presence of a Lewis acid.

Through the incorporation of *o*-terphenyl subunit into poly(aryl ether sulfone)s a linear increase in T_g was observed, yet was lower as compared to the rigid tetrahydro[5]helicene subunit. A similar trend was observed with respect to the solubility of the copolymers and even though high incorporation ratios were unattainable the solubility should only increase. Furthermore, the mechanical properties could not be ascertained due to the limitations in mole % incorporation, however through surface modifications any losses in mechanical properties could be overcome through covalent surface adhesion.

The second issue concerned the effect of increased rotation freedom on the tendency to form macrocyclic oligomers. Through the effective removal of one the

bridge-head methylene groups with the design of **III-3**, an increased tendency to form macrocyclics was observed. The overall effect of macrocyclic formation limited the incorporation of *o*-terphenyl into poly(aryl ether sulfone)s. Also, the appearance of simultaneous polymer growth and degradation while monitoring polymerizations was intriguing. It appears that due to the inherent structure of monomer **III-3** growing chain ends may fold back towards the polymer mainchain and undergo a transesterification reaction. If this postulation is correct, the result would be a macrocyclic oligomer and a growing chain end. The overall effect of cyclodepolymerization and chain growth limits *o*-terphenyl incorporation. Through the manipulation of the method of polymerization, slightly greater incorporation ratios were achieved through a sequential addition of monomers. The addition of **III-3** and BPA, followed by 4-fluorophenylsulfone, allowed for the initial formation of end-capped **III-3** with reactive phenoxides in an effort to reduce the amount of monocyclic oligomers.

III.8 Conclusions

A new A_2X type difluoro-sulfone monomer **III-3** was designed and synthesized, analogous to **II-4**. The structure property relationship of *o*-terphenyl monomers was further understood as direct comparisons were made between poly(aryl ether sulfone)s derived from **III-3** to analogous polymers prepared from **II-4**. It was apparent by not restricting the rotation of *o*-terphenyl ring, as in **II-4**, subsequent incorporation of high contents of **III-3** was difficult due to increasing amounts of macrocyclic oligomers. The polymerization of **III-3** into poly(aryl ether sulfone) was demonstrated up to 20 mole %

feed ratios and the resulting thermal properties increased with increasing mole percentage incorporation. The degree to which the glass transition temperature increased with increasing *o*-terphenyl content was not as great for the analogous bridged *o*-terphenyl containing polymers derived from II-4.

Further derivatization of the latent pyridyl imide group in the polymer backbone via transimidization allowed for the grafting of propargyle imide onto the polymer backbone. Due to the reactive nature of the propargyle imide at high temperatures, the derivatized poly(aryl ether sulfone)s were thermally crosslinked resulting in an insoluble demonstrating the potential for manipulation of processing properties.

The method of polymerization had a direct effect on the percent incorporation of III-3 into poly(aryl ether sulfone)s. Through the sequential addition of 4,4'-isopropylidenediphenol, the resulting mole percent incorporation of III-3 increased from 15 % for III-4c to 16.8 % for III-4d.

The investigation of the ability of polymer III-4d and the like, to undergo transimidization as a route to modifying the surface of an electrode surface was successful. Variations in insulation and surface topology as a result of the method of modification showed to be characterized through the use of both cyclic voltammetry and scanning electron microscopy.

III.9 Experimental Section

Materials.

Benzil, 3-pentanone, maleic anhydride, bromine, 4-fluorobenzenesulfonyl chloride, 2-aminopyridine, propargyl amine and N,N-dimethylacetamide were purchased from Aldrich and used as received. Bisphenol A (BPA) was purchased from Aldrich and recrystallized from toluene prior to use. Monomer grade 4-fluorophenyl sulfone was purchased from Marshallton and used as received.

Measurements.

The monomers and polymers were characterized as outlined in Chapter Two with the following exception. Molecular modeling was performed using HyperChem version 5.01. Models were optimized using the MM+ molecular mechanics method.

3,6-Dimethyl-4,5-diphenylphthalic anhydride III-1.

III-1

Benzil and 3-pentanone were condensed in the presence of aqueous KOH to produce α,β -dimethylanthracetonebenzil⁶ which was then dehydrated with sulfuric acid and acetic anhydride to give 2,5-dimethyl-3,4-diphenylcyclopentadienone.⁷

Sequential reaction with maleic anhydride and elemental bromine gave the final product, 3,6-dimethyl-4,5-diphenylphthalic anhydride.⁸ The purified product **III-1** was obtained as white needles from acetic anhydride. Yield 23 % from benzil; m.p. 280 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.18-7.05 (m, 3H), 6.82 (d, 2H), 2.35 (s, 3H) ppm; ¹³C (100 MHz, CDCl₃) δ 163.3, 150.6, 137.9, 136.7, 129.2, 128.0, 127.7, 127.2, 15.9 ppm; IR (KBr) 1826, 1768 cm⁻¹ (C=O, anhydride); MS (EI, *m/e*, relative intensity %) 328 (M⁺, 100%).

3,6-Dimethyl-4,5-diphenylphthalic(*N*-2-pyridyl) imide **III-2.**

III-2

In a 50 mL 2-necked round-bottomed flask fitted with an Ar inlet/outlet and a Dean-Stark trap, compound **III-1** (10 g, 30.4 mmol) and 2-aminopyridine (2.86 g, 30.4 mmol) were dissolved in 1,2-dichlorobenzene (130 mL) and set to reflux. The reaction proceeded for 16 h at which time IR spectroscopy and TLC indicated complete imidization. The hot reaction solution was poured slowly to 600 mL of hexane. The clear solution deposited off-white platelets of **III-2** upon cooling in an ice bath. The product was filtered, washed with hexanes (3 x 30 mL) and dried at 70 °C under vacuum (5 mmHg) for 24 h. Yield 11.5 g (94 %); m.p. 245 - 248 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.72 (d, 1H), 7.90 (t, 1H), 7.49-7.36 (m, 2H), 7.21-7.11 (m, 6H), 6.93-6.91 (d,

4H), 2.47 (s, 6H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 167.48, 149.51, 149.05, 146.45, 138.61, 138.18, 135.21, 130.5, 129.5, 127.81, 126.89, 123.24, 122.27, 15.81 ppm; IR (KBr) 1770 and 1711 cm^{-1} (C=O, imide); MS (EI, m/e , relative intensity %) 404 (M^+ , 10.2%).

N-2-pyridyl-4',4''-Bis-(4-fluorobenzenesulfonyl)-*o*-terphenyl-3,6-dimethyl-4,5-dicarboxylic imide III-3.

In a flame dried 100 mL 3-necked flask equipped with a condenser, Ar inlet/outlet and a magnetic stirrer, **III-2** (5.0 g, 12.4 mmol) and 4-fluorobenzenesulfonyl chloride (7.18 g, 37.5 mmol) were dissolved in nitrobenzene (25 mL) on heating to 60 °C. Anhydrous AlCl_3 (12.6 g, 98.8 mmol) was added and the reaction was heated to 115 °C and maintained for 24 h. The cooled solution was then added to an aqueous HCl solution (10 % v/v, 200 mL) and allowed to stir vigorously for 18 h. The layers were partitioned and the aqueous layer was extracted with chloroform (3 x 25 mL). The organic phases were combined and concentrated via vacuum distillation and the residue was dissolved in a minimum of chloroform and precipitated into ethanol. The filtrate was concentrated to

yield a second crop of the product. The combined solids were dissolved in a minimum of chloroform and flash chromatographed (SiO₂, 30 g). After washing sequentially with methylene chloride (400 mL) and acetone/hexane (20 % v/v, 600 mL) pure compound **III-3** (a grey amorphous powder) was obtained on removal of the acetone/hexane, which was dried at 100 °C under vacuum (5 mm Hg) for 18 h. Yield: 3.0 g (34 %); m.p. 160 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.64 (d, 1H), 7.84 (t, 1H), 7.79 (q, 2H), 7.63 (d, 2H), 7.38 (d, 1H), 7.31 (t, 1H), 7.20 (t, 2H), 6.97 (d, 2H), 2.34 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 166.9, 166.79, 164.35, 149.54, 146.55, 145.97, 143.43, 140.60, 138.41, 137.03, 137.00, 134.78, 130.53, 130.36, 130.27, 127.35, 123.56, 123.21, 117.05, 116.83, 15.74 ppm; ¹⁹F NMR (300 MHz, CDCl₃) δ -27.42 ppm; IR (KBr) 1774 and 1716 cm⁻¹ (C=O, imide); MS (FAB, *m/e*, relative intensity %) 721.1 (M⁺⁺+H, 9.2%).

Typical Procedure for Copolymerization **III-4a-c**.

BPA (0.5000 g, 2.190 mmol), 4-fluorophenyl sulphone (0.4455 g, 1.752 mmol), **III-3** (0.3137 g, 0.438 mmol), Cs₂CO₃ (0.7564 g, 2.32 mmol) and Mg(OH)₂ (0.0869 g, 1.49 mmol) were placed in a 25 mL 3-necked round-bottomed flask equipped with a magnetic stirrer, Ar inlet/outlet, condenser and Dean-Stark trap. The soluble components were dissolved in DMAc (6.5 mL) and toluene (6.5 mL). The reaction flask was evacuated with Ar for 30 min at which time the mixture was heated to 130 °C (oil bath temperature) for 1.5 h to remove water through azeotropic distillation. The reaction temperature was increased to 165 °C and the solution turned a dark purple color. Polymerization was monitored by GPC and terminated when the measured molecular

weight failed to increase upon subsequent runs. The polymerization solution was cooled and diluted with chloroform and precipitated into methanol. The resulting fibrous polymer was filtered and redissolved in a minimum of chloroform and filtered through a pad of Celite to remove inorganic salts. High molecular weight polymer was obtained by reverse precipitation of this solution using methanol. The obtained fraction was again dissolved into a minimum of chloroform and precipitated into methanol. The obtained polymer was dried at 100 °C under vacuum (5 mm Hg) for 24 h.

Sequential Addition Copolymerization of III-4d.

BPA (0.5000 g, 2.190 mmol), compound III-3 (0.3137 g, 0.438 mmol), Cs_2CO_3 (0.7564 g, 2.32 mmol) and $\text{Mg}(\text{OH})_2$ (0.0869 g, 1.49 mmol) were placed in a 25 mL 3-necked round bottom flask, equipped with a magnetic stirrer, Ar inlet/outlet, condenser and Dean-Stark trap. The soluble components were dissolved in DMAc (6.5 mL) and toluene (6.5 mL). The reaction flask was evacuated with Ar for 30 min at which time the mixture was heated to 130 °C (oil bath temperature) for 1.5 h to remove water through azeotropic distillation. The reaction temperature was increased to 165 °C and the solution turned a dark purple color. After 2 h, TLC showed the absence of III-3, at which time 4-fluorophenylsulfone (0.4455 g, 1.752 mmol) was added. The polymerization was monitored by GPC and terminated when the measured molecular weight failed to increase upon subsequent runs. The polymerization was terminated and worked up as described above. The obtained polymer was dried at 100 °C under vacuum (5 mmHg) for 24 h.

Stoichiometric Offset Copolymerization of III-4e.

The same procedure described above for 4a-c was used except the initial stoichiometry of III-3 (0.4818 mmol) was offset such that an excess was present. The stoichiometry of BPA (2.190 mmol) and 4-fluorophenylsulfone (1.752 mmol) were unchanged.

3,6-Dimethyl-4,5-diphenylphthalic(N-3-propyne) imide III-5. **III-5**

In a 25 ml, 3-necked round-bottomed flask fitted with a condenser and Ar inlet/outlet, compound III-2 (200 mg, 0.50 mmol) and propargylamine (52 mg, 0.51 mmol) were dissolved in DMAc (5 mL) and stirred at 70 °C for 16 h. The reaction mixture was precipitated into methanol/water (20 mL, 9/1) containing HCl (1 mL). The resulting white solid was filtered and dried overnight under vacuum (5 mm Hg) at 60 °C. Yield: 135 mg (74 %); m.p. 192 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.21-7.12 (m, 6H), 6.91 (d, 4H), 4.49 (d, 2H), 2.44 (s, 3H), 2.25 (t, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 166.82, 147.62, 137.53, 133.76, 128.43, 127.00, 126.76, 125.82, 76.64, 70.07, 25.69, 14.70 ppm; IR (KBr) 1764 and 1708 cm⁻¹ (C=O, imide); MS (EI, *m/e*, relative intensity %) 365 (M⁺, 100%).

Post Polymerization transimidization.

The same conditions were employed as for the preparation of compound **III-5**. Propargylamine (0.2 mL) was added to a solution of **III-4d** (100 mg) in DMAc (2 mL) and the solution was heated at 75 °C for 18 h. The resulting polymer **III-5d** was isolated by precipitation into methanol/water (20 mL, 9/1) containing HCl (1 mL). The obtained polymer was dried at 100 °C under vacuum (5 mm Hg) for 24 h.

III.10 References

- 1) MacKinnon, S. M.; Wang, Z. Y.; *Macromolecules*, **1998**, *31*, 7970.
- 2) Takekoshi, T.; Kochanowski, J.E. US patent, **1974**, 3,850,885.
- 3) Webb, J.L. European patent, **1984**, 132547.
- 4) Webb, J.L. U.S. Pat. 4,578,470 (1986).
- 5) Rogers, M.E.; Glass, T.E.; Macham, S.J.; Rodrigues, D.; Wilkes, G.L.; McGrath, J.E.
J. Polym. Sci., Part A: Polym. Chem., **1994**, *32*, 2663.
- 6) Herbert, C. G.; Hay, A. S.; *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 1095.
- 7) Bender, T. P.; Wang, Z. Y. *PMSE*, **1990**, *80*, 120.
- 8) (a) Allen, C. F. H.; Van Allan, J.; *J. Am. Chem. Soc.*, **1942**, *64*, 1260. (b) Grummitt,
O.; *Org. Syn. Coll.* **1955**, *3*, 807.
- 9) Japp, F. R.; Meldrum, A. N.; *J. Chem. Soc. Trans.*, **1901**, *79*, 1024.
- 10) Gray, F. W.; *J. Chem. Soc.*, **1909**, *95*, 2134.
- 11) Fuchs, B.; Pasernak, M.; *J. Chem. Soc. Chem. Comm.*, **1977**, 537.
- 12) Carter, K.; *Macromolecules*, **1995**, *28*, 6462.
- 13) Martinez, C. A.; Hay, A. S.; *J. Polym. Sci. Part A: Polym. Chem.*, **1997**, *35*, 2015.
- 14) Jennane, J.; Boutros, T.; Giasson., *Can. J. Chem.* **1996**, *74*, 2509.
- 15) Ulman, A.; *Characterization of Organic Thin Films*; 1 ed.; Butterworth-Heinemann:
Toronto, 1994.

CHAPTER FOUR: FUNCTIONAL POLY(ARYL ETHER IMIDE)S DERIVED FROM A 3,6-DIAMINO NAPHTHALIMIDE

IV.1 Introduction

The family of poly(aryl ether imide)s has been postulated to be one of the most important high-performance polymers.¹⁻⁴ The excellent electrical, thermal and antflammable properties have been exploited as poly(aryl ether imide)s generally have improved processability over wholly aromatic polyimides. However, application of poly(aryl ether imide)s continue as structural in nature as well as protective coatings in the electronic industry. The application as photonic materials has recently emerged as polymer waveguides and patterning become very important. Through the design of an A₂X-type monomer containing a reactive functional group suitable for grafting and crosslinking, photopatternable poly(aryl ether imide)s may be attainable.

As previously shown, the A₂X-type difluorosulfone monomers II-4 and III-3 containing *o*-terphenyl subunits, led to functionalizable poly(aryl ether sulfone)s.^{5,6} However, the major pitfall of the *o*-terphenyl monomers involved the formation of increasing amounts of macrocyclic oligomers with increasing mole percent feed ratios. Through the design of a diamine monomer that reduces the amount of free rotation available to the polymerizable units, the tendency for macrocyclic formation should be

diminished. The use of a fused ring system where both “A” and the inert “X” functionality are attached, would remove the free rotation of the reactive groups. The use of A_2X -type monomers for the preparation of functional polyimides has arisen in the literature, with the preparation of nonlinear optical side chain soluble polyimides.⁷ Through the use of 2,4-diaminophenol dihydrochloride (Aldrich Chemical Company), hydroxy-containing, soluble polyimides were prepared. The free phenol groups were derivatized with either diazo- and stilbene-based chromophores (Figure IV.1). This methodology has also been used by the incumbent’s co-workers, in the preparation of polyimides from 3,5-diaminobenzoic acid, allowing for further grafting and crosslinking.⁸

Figure IV.1 Polyimide and poly(aryl ether imide) derived from a commercial A_2X -type monomer⁷

The further development of the A_2X -type monomers addresses one of the overall objectives of this thesis, namely to concurrently increase T_g while maintaining or

increasing solubility or processing. In order to minimize cyclic formation the naphthalene core is chosen, as it is the smallest fused ring system. The development of A₂X-type monomers requires the choice of latent reactive group. The use of anhydride groups as routes to incorporating functionality into the poly(aryl ether)s was successfully shown with the preparation of II-4 and III-3 and remains the preferred choice. However, the choice of inert functionality needs to be addressed in more detail, as saponification or transimidization of the polymer may lead to complications. Saponification would lead to extensive chain degradation, as the polymer backbone consists of labile imide groups and transimidization has not been documented to occur with naphthalimides, but readily occurs in phthalimides which would also lead to chain degradation. The solution to probable chain degradation lies in the development of a monomer that contains functional groups inert to polymerization conditions. Therefore, through the use of ethanolamine, naphthalimides can be prepared that have free hydroxy groups present and may be further functionalized to facilitate polymer patterning.

Naphthalimides have generally been incorporated into polymeric systems through two general methods: (1) the incorporation as pendent functionalities on vinyl polymers⁹⁻¹⁵ and (2) the direct polymerization of suitable monomers leading to incorporation directly into the mainchain of the polymer¹⁶⁻²⁰ (Figure IV.2). The latter method has generally been achieved through the polymerization of either naphthalic dianhydrides or bisnaphthalimides containing reactive acetylene or activated halogens.

Figure IV.2 General methods employed to incorporate naphthalimides into polymers

As previously outlined, a limited number of poly(aryl ether)s have been prepared from monomers that deviate from *para, para* – substitution. The realization of 3,6-diaminonaphthalimide-based A_2X -type monomer resulted, as a route to preparing both poly(aryl ether imide)s and polyimides through facile polycondensation with reactive dianhydrides.

IV.2 Monomer Synthesis and Characterization

The facile synthesis of monomer IV.3 was accomplished in three steps from commercially available materials (Scheme IV.1). The initial dinitration of 1,8-naphthalic

anhydride was accomplished through the addition of a mixture of nitric and sulfuric acids to a solution of the starting anhydride in acetic acid. The 3,6-dinitro-1,8-naphthalic anhydride IV.1 was obtained in high yield after recrystallization from toluene, as determined through conventional characterization and compared to the literature procedure of Hodgson and Ward in 1945.²¹

Scheme IV.1 Synthesis of A₂X-diamino-hydroxy monomer IV.3

The hydrogenation of dinitro anhydride IV.1 was based on reported procedures for the reduction of 4-nitro-1,8-naphthalic anhydride to 4-amino-1,8-naphthalic anhydride.²² The catalytic hydrogenation was accomplished in high yield through the action of Pd/C (10 wt %) under 50 psi of hydrogen, to yield 3,6-diamino-1,8-naphthalic anhydride (IV.2). The ¹H NMR spectrum of IV.2 showed the expected two aromatic resonances similar to that of IV.1, with a prominent shift from 9.78 and 9.07 ppm to 7.59 and 7.01 ppm due to the difference in electron withdrawing effects of the nitro moiety compared to the donating effects of the amino groups. The appearance of a broad singlet at 5.84 ppm, having an integration twice that of the aromatic resonances, was attributed to the amino protons in the 3,6- positions (Figure IV.3a). The ¹³C NMR spectrum also showed the correct number of resonances for seven magnetically different carbon atoms

(Figure IV.3b). The high resolution mass spectrum analysis gave rise to a parent ion of 228 mass units corresponding to the molecular formula of IV.2.

Another important consideration is the stability of IV.2 as it contains both an anhydride and an amine that usually react together through nucleophilic imidization. The reactivity of naphthalic anhydride is decreased compared to the 5-membered phthalic anhydride and usually does not react with aromatic amines below 140 °C.^{17,23} The stability of 4-amino-1,8-naphthalic anhydride is known as it available from Aldrich Chemical Company (CAS 6492-86-0). However, naphthalic anhydrides can be converted to the corresponding naphthalimides with ease when aliphatic amines are used.²⁴

Figure IV.3 (A) ^1H NMR spectrum of IV.2 and (B) ^{13}C NMR spectrum of IV.2

Accordingly, the selective imidization of IV.2 using ethanolamine was accomplished at room temperature in absolute alcohol. The resulting imide IV.3 was of the A₂X-type and of monomer quality directly from reaction. Through conventional characterization methods the structure was verified. The ¹H NMR spectrum revealed the expected pattern and relative integration of the aromatic protons compared to those of the amine as in the precursor compound. The appearance of two triplets at 3.58 and 4.10 ppm and a broad singlet at 4.83 ppm represented the ethylene and hydroxy protons in the correct integration. The ¹³C NMR spectrum also showed the appearance of two aliphatic carbons at 41.5 and 57.7 ppm along with the expected seven magnetically different aromatic carbons. The successful imidization was also evident upon analysis of the IR spectrum showing a shift in the carbonyl region from 1769 and 1729 cm⁻¹ of the precursor anhydride to 1708 and 1668 cm⁻¹ characteristic of a naphthalimide. The Mass Spectrum also revealed the correct parent ion of 271 mass units, in greatest abundance.

IV.3 Polymer Synthesis and Characterization

The polymerization of the A₂X – type diamino monomer IV.3 was demonstrated through the preparation of both a poly(aryl ether imide) and a polyimide. The variation in the choice of anhydride allowed for the preparation of either a poly(aryl ether imide), from BPADA or a polyimide, from 6FDA (Scheme IV.2). The two polymerizations were carried out in *m*-cresol at 200 °C and monitored by GPC until subsequent molecular weights were measured to be consistent after 36 hrs.

Scheme IV.2 Polycondensation of IV.3 with BPADA and 6FDA to give IV.4 and IV.5 respectively

Polymerization times using oxy-dianiline (ODA) or methylene dianiline (MDA) are generally on the order of a few hours compared to 36 hours for the polymerization of IV.3 with BPADA or 6FDA. Through the comparison the nucleophilicity of the aromatic diamines the relationship to the subsequent polymerization rate may be ascertained through the NMR analysis of the chemical shift of the amine protons.^{25,26} The location of amine proton resonance gives an indication to the electronic environment and the subsequent electron donating abilities of the amine. As a result, the more upfield the resonance the greater the basicity of the amine and the faster the polymerization. For example, reactive commercial diamines such as ODA and MDA have amine hydrogen chemical shifts of 4.76 and 4.78 ppm in dimethyl sulfoxide, corresponding to fast polymerization times on the order of a few hours. Upon substitution of the electron donating effects of methylene and ether linkages with electron withdrawing groups such as sulfone or carbonyl groups, less reactive amines result with chemical shifts of 5.99 and 5.89, respectively. Due to the electron withdrawing nature of the imide functionality,

the diamino naphthalimide IV.3 has an amine chemical shift of 5.70 ppm in dimethyl sulfoxide resulting in extended polymerization times (Table IV.1).

Table IV.1 Comparison of NH_2 ^1H NMR chemical shifts of diamines

Diamine	$\delta \text{ NH}_2$ ppm
4.76
4.78
5.99
5.89
IV.3	5.70

The hydroxy containing poly(aryl ether imide) IV.4 had an apparent average molecular weight of 21 300 g/mol with a polydispersity of 2.4 by GPC. Polymer IV.4 was soluble in polar aprotic solvents as well as chloroform and had a measured inherent viscosity of 0.30 dL/g in NMP at 30°C. The presence of free hydroxyl groups was determined by IR spectroscopy showing a peak at 3360 cm^{-1} . IR spectroscopy also

confirmed the presence of both phthalimide at 1770 and 1720 cm^{-1} and naphthalimide at 1709 and 1668 cm^{-1} .

Figure IV.4 DSC of polymer IV.4

Poly(aryl ether imide) IV.4 had a measured T_g of 249 °C by DSC (Figure IV.4) and thermal decomposition temperature of 430 °C as measured by TGA. The contributions of the naphthalimide monomer to the measured thermal properties may be determined upon comparison of the properties of IV.4 to poly(aryl ether imide)s prepared from the same anhydride and 1,3-diaminophenylene (Utem™) or ODA (Table IV.2). The glass transition temperature of Utem™ has been reported to be 213 °C, while the corresponding poly(aryl ether imide) from ODA has a T_g of 223 °C.¹ The increase in T_g

for IV.4 can be attributed to the greater aromaticity of the fused naphthalene derivative and it's the increased chain rigidity.

Table IV.2 Comparison of poly(aryl ether imide)s derived from BPADA

isomer	$T_g(^{\circ}\text{C})^a$	$T_d(^{\circ}\text{C})^b$
Ultem™	4,4'	215	508
		3,3'	236	534
ODA	4,4'	223	537
		3,3'	235	520
4,4'	249	430

^a measured by DSC.

^b measured by TGA (5% weight loss).

The polycondensation of IV.3 with 6FDA afforded an hydroxy-containing polyimide IV.5 with a measured apparent average molecular weight of 10 300 g/mol with a similar polydispersity of 2.4 by GPC. Thermal analysis of IV.5 showed a 5% weight loss at 435 °C under nitrogen by TGA and a T_g of 314 °C as measured by DSC (Figure IV.5). Polymer IV.5 was soluble in polar aprotic solvents but only slightly soluble in chloroform, with a measured inherent viscosity of 0.24 dL/g in NMP at 30 °C. The presence of free hydroxyl groups was determined by IR spectroscopy.

Figure IV.5 DSC of polymer IV.5

The comparison of the physical properties of polyimide IV.5 with commercially available polyimides based on 6FDA, is of interest as fluorinated polyimides such as 6FDA-ODA have recently been under investigation as waveguide materials.²⁷⁻²⁹ The thermal properties of polyimide IV.5 may be discussed in comparison to reported glass transitions temperatures of some 6FDA containing polyimides (Table IV.2).³⁰ The 6FDA-ODA polyimide has a T_g of 285 °C, which is within a few degrees of the T_g of 291 °C for 6FDA-MDA polyimide. These values reported do not contain any viscosity data leading to the assumption that a high molecular weight was achieved. Comparison to a naphthalene-containing polyimide derived from 1,6-diaminonaphthalene and 6FDA, the T_g of 365 °C indicates a dramatic effect that a fused ring can have on T_g . Polyimide

IV.5 had a T_g of 314 °C owing to increased aromaticity and chain rigidity over the polyimides derived from ODA and MDA. However, decreases in T_g compared to the naphthalene-6FDA polyimide indicates that the alkyl naphthalimide may reduce the T_g of the polymer.

Table IV.2 Comparison of polyimides derived from 6FDA

Ar	$T_g(°C)^a$
ODA	285
MDA	291
NDA	365
314

IV.4 Post Polymerization Transformation and Characterization

The formation of an ester generally involves the nucleophilic reaction of an alcohol and an acid chloride.³¹ The presence of cinnamate esters is of general interest because it provides a route to photocurable polymers.³² The cinnamate moiety has proven to be reactive in solution, yet less effective in the solid state due to the required overlap of vinyl groups to facilitate [2 + 2] cycloaddition. Thus, the facile conversion of the free alcohols of IV.4 to cinnamate esters by treatment with cinnamoyl chloride was carried out in DMF in the presence of triethylamine (Scheme IV.3). The derivatized polymer IV.6 was isolated from 10 % aqueous methanol, redissolved in chloroform and filtered to remove insoluble solids.

Scheme IV.3 Post polymer esterification of IV.4 to give polymer IV.6

The characterization of cinnamate functionalized polymer IV.6 proved to be difficult, as general methods of IR and UV/Vis spectroscopies resulted in ambiguity. The appearance of an asymmetric double stretch corresponding to ethyl cinnamate generally appear around 1638 cm^{-1} in the IR spectrum, however the parent polymer IV.4 has extensive stretches in this region. The same holds true for the UV/Vis spectrum, as the general absorbency of naphthalimides overshadowed the spectral range of cinnamate esters. The resulting evidence available was indirect in nature. The IR spectrum of functionalized poly(aryl ether imide) IV.6 showed the absence of OH stretching (Figure

IV.6) indicating the ester formation. Furthermore, the cinnamate polymer IV.6 had a lower T_g (214 °C) than that of IV.4 and a decomposition temperature of 320 °C, supporting the functionalization as a long aliphatic groups that usually results in lowered T_g and decreased thermostability. The GPC chromatogram of IV.6 had the same retention time and polydispersity indicating that no thermal degradation occurred. The last piece of evidence came from the photopatterning experiment, as cinnamates are known to crosslink under UV irradiation (300-350 nm). A thin film of approximately 300 nm in thickness, as determined by ellipsometry, was spin coated onto a silicon wafer. The film was placed under a UV spot light (Nova Cure Station) for 1-2 minutes and developed in DMAc, resulting in a visible pattern on the silicon surface. Since polymer IV.6 is photopatternable, the cinnamate ester must be present. In order to have more concrete evidence, a measurement was required to confirm that the polymer had actually crosslinked.

Figure IV.6 IR Spectra of parent polymer IV.4 and functionalized polymer IV.6

The functionalized polymer IV.6, as well as polymers IV.4 and IV.5 were each dissolved in DMF and films were cast of approximately 10 microns in thickness. The small pieces of the free standing films were treated with UV irradiation in the same manner as the spin coated films, however a longer duration was required owing to the increased thickness of the cast films. The cured films were then subjected to DSC thermal analysis where it was observed that only the cinnamate containing polymer IV.6 showed an increase in T_g . The T_g of both hydroxy containing polymers IV.4 and IV.5 remained unchanged after multiple DSC scans, where as the cinnamate polymer IV.6 had a T_g of 214 °C for the first scan with an slight exotherm above the T_g . The subsequent scans showed a very small endothermic transition at 228 °C owing to an increase in T_g (Figure IV.7), indicating that polymer IV.6 was thermosetting.

Figure IV.7 DSC scans of polymer IV.6 after UV irradiation

The general use of polymers has greatly extended into the electronic environment beyond general packaging and structural applications. Investigations into high performance polymers as organic waveguide materials has currently acquired a great deal of research efforts both academically and commercially.³³⁻³⁹ The enhanced fabrication that spin coating and dip coating offer compared to chemical vapor deposition (CVD) and the ability for the tuning of the refractive index, are the general reasons for the intense interest. Surfaces have been patterned using microlithographic methods such as ion-

beam etching, which are destructive in nature. There have been a few examples of UV photopatternable polymer light emitting devices based on poly(phenylene vinylene)s³³ and polythiophenes³⁴. Polymer-based waveguide devices for wavelength division multiplexers (WDM) have also been demonstrated through the use of acrylate monomers.³⁵

IV.6 Conclusions

The extension of the A₂X methodology to afford poly(aryl ether imide)s and polyimides has been successful through the design, synthesis and polymerization of N-(2-hydroxyethyl)-3,6-diamino-1,8-naphthalimide, IV.3. The successful imidization with either BPADA or 6FDA gave a poly(aryl ether imide) and polyimide, respectively. The rigid aromatic nature of the naphthalimide led to a measurable increase in T_g when compared to polymers prepared from the same dianhydride with commercial diamines, such as ODA and MDA.

Further derivatization of the hydroxyl containing poly(aryl ether imide) IV.4 with cinnamoyl chloride allowed for the formation of pendent phenyl acrylate units (IV.6), with a decreased T_g of 214 °C. The subsequent photocuring increased the T_g to 228 °C after the first scan, owing to thermal crosslinking. The ability to form photopatterns on silicon wafers demonstrated that polymer IV.6 has uses either as a resist or potentially a directly patternable polymer waveguide. The ability to photopattern polymers has become of great importance in the process design of commercial products.

IV.7 Experimental Section

Materials

3,6-Dinitronaphthalic anhydride was prepared according to the reported procedure of Hodgson and Ward.²¹ Naphthalic anhydride, Pd/C 10 wt%, ethanolamine, triethylamine, cinnamoyl chloride, DMF and *m*-cresol were purchased from the Aldrich Chemical company and used as received. Monomer grade BPADA and 6FDA were purchased from Kriskiev and used as received.

All deuterated solvents were purchased from Canadian Isotopes Incorporated and used as received.

Measurements

The monomers and polymers were characterized a outlined in Chapter Two.

Monomer Synthesis

IV.2

In a 500 ml hydrogenation flask were suspended 3,6-dinitronaphthalic anhydride IV.1 (5.00 g, 0.017 mol) and Pd/C 10 wt% (1 g) in DMF (100 ml) and ethanol (95 %, 50 ml). The reaction flask was evacuated twice with hydrogen and placed under pressure (50 psi) and shaken. During the first two hours, the hydrogen pressure was continually reestablished. After 24 hours the reaction was complete and the mixture was filtered to

remove the catalyst. The collected solids were washed with DMF (100 ml) and the combined filtrates were rotary evaporated, and dried under high vacuum at 150 °C for 24 hours. Yield: 3.5 g (0.015, 90 %); m.p. >300 °C; ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 7.59 (d, 2H, $J_{\text{H-H}} = 2$ Hz), 7.01 (d, 2H, $J_{\text{H-H}} = 2$ Hz), 5.84 (s, NH_2) ppm; ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ 161.1, 147.8, 135.5, 118.7, 118.3, 116.7, 110.3 ppm; IR (KBr) 3500 and 3450 cm^{-1} (NH_2) 1760 and 1729 cm^{-1} (C=O , anhydride); MS (EI, m/e , relative intensity %) 228 (M^+ , 100%).

In a 100 ml round-bottomed flask fitted with a condenser and a magnetic stir bar was suspended IV.2 (2.00 g, 8.77 mmol) in absolute ethanol (50 ml). Ethanolamine (0.8 ml, 13.2 mmol) was added dropwise via a syringe and the suspension was stirred overnight at 60°C. The solids were filtered and dried under high vacuum at 100 °C for 24 hrs. Yield: 2.1 g (7.75 mmol, 88 %); m.p. 300-305 °C; ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 7.59 (d, 2H, $J_{\text{H-H}} = 2.0$ Hz), 6.93 (d, 2H, $J_{\text{H-H}} = 2.0$ Hz), 5.70 (s, NH_2), 4.83 (s, 1H, OH), 4.10 (t, 2H, $J_{\text{H-H}} = 6.6$ Hz) 3.58 (t, 2H, $J_{\text{H-H}} = 6.6$ Hz) ppm; ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ 163.9, 147.5, 135.4, 122.3, 116.8, 114.4, 109.4, 57.7, 41.5 ppm; IR (KBr)

3500 and 3450 cm^{-1} (NH_2) 3300 (OH) 1709 and 1668 cm^{-1} ($\text{C}=\text{O}$, imide); MS (EI, *m/e*, relative intensity %) 271 (M^{++} , 100%).

Typical Method for Polycondensation

In a 100 ml 3-necked round-bottomed flask, were charged diamine IV.3 (0.8000 g, 2.949 mmol) and BPADA (1.5349, 2.949 mmol) in *m*-cresol (45 ml, ~5 % wt/v) and heated to 200 °C. The polymer growth was monitored by GPC (CHCl_3) and the polymerization was terminated after subsequent measurements showed no change (36 hrs). The polymerization pot was diluted with *m*-cresol (50 ml), cooled to ~ 60 °C and precipitated into acidic methanol (10% HCl, 800 ml). The polymer was collected on a sintered glass filter, dissolved in DMF (50 ml) and reverse precipitated with methanol. The coagulated polymer was filtered, dissolved in a minimum of DMF and precipitated into methanol, filtered and dried under high vacuum at 190 °C for 48 hrs.

Post Polymerization Reaction and Transformation

In a 50 ml 2-necked round-bottomed flask, fitted with a magnetic stir bar and nitrogen inlet/outlet, were dissolved polymer IV.4 (0.50 g, 0.69 mmol OH) and triethylamine (0.70 g, 0.69 mmol) in DMF (10 ml). Cinnamoyl chloride (0.115 g, 0.69 mmol) was added dropwise via a syringe over 10 minutes. The reaction was stirred overnight at room temperature and precipitated into aqueous methanol (10%, 500 ml). The solids were filtered, redissolved in chloroform and the insoluble solids were removed. The chloroform solution was concentrated and precipitated into methanol,

where cinnamate polymer IV.6 was collected on a sintered glass filter and dried at 100 °C overnight. Yield : 370 mg

IV.8 References

- 1) Takekoshi, T.; Kochanowski, J. E.; Manello, J. S.; Webber, M. J. *J. Polym. Sci. Polym. Symp.* **1986**, *74*, 93.
- 2) Eastmond, G. C.; Paprotny, J. *Reactive & Functional Polymers*, **1996**, *30*, 27.
- 3) Im, K. J.; Jung, J. C., *J. Polym. Sci. A: Polym. Chem.*, **1999**, *38*, 402.
- 4) Kim, W-G.; Hay, A.S., *Macromolecules*, **1993**, *26*, 5275.
- 5) MacKinnon, S. M.; Wang, Z. Y., *Macromolecules*, **1998**, *31*, 7970.
- 6) MacKinnon, S. M.; Bender, T. P.; Wang, Z. Y., *J. Polym. Sci. A: Polym. Chem.* **2000**, *38*, 9.
- 7) Lee., H-J., Lee, M-Y., Han, S. G., Kim, H-Y., Ahn, J-H., Lee, E-I., Won, Y. H., **1998**, *36*, 301.
- 8) Kuang, L and Wang, Z. Y., unpublished results.
- 9) Bouche, C. M., Le Barny, P., Facoetti, H., Robin, P., *Appl. Phys. Lett.*, **1988**, *73*(3), 879.
- 10) Cacialli, F.; Friend, R. H.; Bouche, C. M.; Le Barny, P.; Facoetti, H.; Soyer, F.; Robin, P., *Appl. Phys. Lett.*, **1988**, *83*(3), 2343.
- 11) Grabchev, I.; Bojinov, V., *Polym. Degrad. and Stabil.*, **2000**, 147.
- 12) Tian, H.; He, Y.; Chang, C.P., *J. Mater. Chem.*, **2000**, *10*, 2049.
- 13) Konstantinova, T.; Grabchev, I., *J. Appl. Polym. Sci.*, **1996**, *62*, 447.
- 14) Du, F.S.; Cai, H., Li, Z. C.; Li, F-M., *J. Polym. Sci. A: Polym. Chem.* **1998**, *36*, 1111.
- 15) Filipova, T. Z.; Grabchev, I.; Petkov, I. *J. Polym. Sci. A: Polym. Chem.* **1997**, *35*, 1069.

- 16) Melissaris, A. P.; Morton, H. L., *Polymer*, **1994**, 35(5), 3305.
- 17) Sonpatki, M. M.; Skaria, S.; Fradet, A.; Ponrathnam, S.; Rajan, C. R., *Polymer*, **1999**, 40, 4377.
- 18) Michot, C.; Baril, D.; Armand, M., *Solar Energy and Solar Cells*, **1995**, 39, 289.
- 19) Ghassemi, H.; Zhu, J. H., *J. Polym. Sci. B: Polym. Phys.*, **1995**, 33, 1633.
- 20) Viehbeck, A.; Goldberg, M. J.; Kovac, C. A., *J. Electrochem. Soc.*, **1990**, 137(5), 1460.
- 21) H. H. Hodgson and E. R. Ward, *J. Chem. Soc.*, **1945**, 590.
- 22) Middleton, R. W.; Parrick, J.; Clarke, E. D.; Wardman, P., *J. Heterocyclic Chem.*, **1986**, 23, 849.
- 23) Sek, D.; Wanic, A.; Schab-Balcerzak, E., *J. Poly. Sci., Part A Polym. Chem.* **1995**, 33, 547.
- 24) Middleton, R. W.; Parrick, J., *J. Heterocyclic Chem.*, **1985**, 22, 1567.
- 25) Ando, S.; Matsuura, T.; Sasaki, S., *J. Poly. Sci., Part A Polym. Chem.* **1992**, 30, 2285.
- 26) Bordwell, F., *Acc. Chem. Res.*, **1988**, 21, 456.
- 27) Trigaud, T.; Aubry, C.; Chiron, D.; Moliton, J. P.; Colombeau, B., *Synth. Met.*, **2000**, 110, 33.
- 28) Han, K.; Lee, H.-J.; Rhee, T. H., *J. Appl. Polym. Sci.*, **1999**, 74, 107.
- 29) Han, K.; Jang, W.-H.; Rhee, T. H., *J. Appl. Polym. Sci.*, **2000**, 77, 2172.
- 30) Ohya, H., Kudryavtsev, V. V., Semenova, S. I., *Polyimide membranes – Application, Fabrications and Properties*; 1st Ed.; Gordon and Breach Publishers: Netherlands, **1996**. p 83.

- 31) March, J., *Advanced Organic Chemistry*, 3rd Ed. John Wiley & Sons, Inc.: Canada, 1985. p 346.
- 32) (a) Reiser, A.; Egerton, P. L., *Macromolecules*, **1979**, *12*, 670. (b) Egerton, P. L.; Pitts, E.; Reiser, A., *Macromolecules*, **1981**, *14*, 95.
- 33) Tada, K.; Onoda, M.; Nakayama, H., *Jpn. J. Appl. Phys. Part 2*, **1999**, *38(7B)*, L833.
- 34) Tada, K.; Onoda, M.; Nakayama, H., *Jpn. J. Appl. Phys. Part 2*, **1998**, *37(10A)*, L1181.
- 35) Viens, J. F.; Callender, C. L.; Noad, J. P.; Eldada, L.; Norwood, R. A., *SPIE*, **1999**, *3799*, 202.

CHAPTER FIVE: ELECTROCHROMIC POLY(ARYL ETHER)S DERIVED FROM PERYLENE AND NAPHTHALENE DIIMIDES

V.1 Introduction

Poly(aryl ether)s have maintained conventional applications in medical and food processing equipment, wire/cable insulation and automotive parts, which are “passive” in nature. Materials have generally been classified as either “passive” and “active” with respect to the application. A material may be classified as “passive” if while performing the function required, no changes to the physical properties of the polymer occur. On the other hand, a material can be classified as “active” if while providing the function of interest, the physical properties change allowing for detection between different states. For example, an “active” material may undergo molecular level interactions that induce changes in the bulk properties of the material, such as absorption wavelength, refractive index or electrical conductivity.

In recent years, considerable interest has been directed towards the development of electrochromic polymers for use in smart windows, information displays and variable-reflectance mirrors (Figure V.1).¹ Electrochromic behavior can be defined as the change

Figure V.1 Applications of electrochromic materials

in optical properties upon the application of an electric field, where upon reversal of the field the original state returns. Commercial applications of electrochromic materials have mainly consisted of solid state devices allowing for the action of an electric field through transparent electrodes. A schematic of an electrochromic sandwich cell is shown in Figure V.2, which outlines the general layers required in order to have a functioning electrochromic device (ECD).² The premise of a dual polymer ECD is to have electrochromic materials that are complimentary and change to similar colors while in opposite electrochemical states. The cross-section of the ECD shows how the two complimentary electrochromic materials, which have been coated on a transparent indium tin oxide coated glass electrode (ITO), sandwich a polymer gel electrolyte. The

polymer deposition usually involves either spin coating, dip coating or through direct electropolymerization.

Figure V.2 Generic representation of dual polymer ECD sandwich cell
(from <http://www.chem.ufl.edu/~polymer/reynlds/condpoly.htm>)

In general, there exists three major classes of materials that are used as electrochromic materials in the construction of ECDs, including metal oxides, conjugated polymers and molecular dyes.² Metal oxide films have generally been prepared from tungsten oxide, nickel oxide or molybdenum oxide. Thin films have been prepared on optically transparent electrodes through sputter coating, electrochemical or sol-gel techniques. The electrochromic behavior of metal oxide films is dependent on pH, moisture and exposure to the atmosphere. The switching speeds of crystalline metal oxide films are normally slow, on the scale of 15-60 s for the complete conversion to either the bleached or colored states.

Organic molecular dyes have often been deposited onto optically transparent electrodes directly or have also been dispersed throughout the electrolyte of an

electrochemical cell. One of the most commonly used molecular dyes is Prussian Blue, which has relatively fast switching speeds (20 ms) when deposited as electrode confined films. On the occasion when the dye has been dispersed into the electrolyte, the switching speeds are slowed due to the required diffusion to the electrode surface.

The class of conjugated polymers used in ECDs are normally of the p-doping type such as polythiophene, polyaniline and polypyrrole. There has been limited work on n-doped electrochromic polymers. If a species undergoes an oxidation upon application of a positive bias it may be generally termed “p-doping” or “anodically coloring”, meaning the material has been populated with positively charged centers. For example, poly(3-alkylthiophene)s are generally red to orange in the neutral state, where upon oxidation become deep blue or violet in color (Figure V.3). Conversely, if a species undergoes a reduction to give a material that is colored, it is called an “n-doping” or “cathodically coloring”. The terminology of anodic and cathodic coloring materials, originates from which electrode the material is in contact with. There is a general void of “n-doping” electrochromic materials which has been filled by “p-doping” materials that change color upon reduction of the corresponding oxidized states. For example, poly(3,4-ethylenedioxythiophene) is dark blue-violet colored in the neutral state and transparent light blue in the oxidized state and is therefore a “p-doping” because it undergoes oxidation reactions from the neutral state (Figure V.3). However, because the polymer changes color upon reduction to the neutral state, the material is cathodically coloring, and filling the void of needed organic based “n-doping” materials.

Figure V.3 Examples of anodically and cathodically coloring “p-doping” polythiophenes

The search for “n-doping” polymers has led to aromatic imides derived from 3,4,9,10-perylenetetracarboxylic dianhydride (PTDA) and 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA). Both aromatic diimides have been reported to undergo two reversible one-electron reductions (Figure V.4).³ The perylene diimides have been studied in field-effect transistors and Schottky diodes, resulting in evidence for n-type conduction.⁴ Perylene diimides have also been investigated as electron transport materials for electroluminescent (EL) devices through blending with poly(N-vinyl carbazole)⁵ and photoconductors in xerography.⁶

Figure V.4 Two one-electron reductions of naphthalene and perylene diimides

It is well known that aromatic polyimides generally show rather poor solubility in organic solvents, especially for those derived from rigid dianhydrides such as PTDA and NTDA. Thus, to incorporate the rigid perylene diimide into a polymer, one must use either a flexible, aliphatic, low T_g polymer such as polyethylene glycol as a base polymer⁷ or copolymerize the perylene-based monomer with others. In the latter case, our lab has previously demonstrated that perfectly alternating copolyimides can be prepared by a one-step solution polymerization using a perylene diimide diamine, prepared from PTDA and an excess of a long chain alkyl diamine, and an aromatic dianhydride.⁶

Conceivably, rigid perylene diimide and naphthalene diimides could be incorporated into amorphous poly(aryl ether)s if PTDA and NTDA are converted to the appropriate diimide monomer. The preparation of a bisphenol monomer analogous to BPA should yield monomers of similar reactivity suitable for copolymerization (Figure V.6).

Figure V.5 Synthesis of alternating perylene containing polyimides.⁶

Figure V.6 Proposed electrochromic bisphenol monomers for polycondensation etherification

V.2 Monomer Synthesis and Characterization

The direct imidization of PTDA was achieved in a good yield with a slight excess of 4-amino-4'-hydroxy-isopropylidenediphenol⁸ (A-BPA) in refluxing NMP using zinc acetate as a catalyst (Scheme V.1). The reaction mixture slowly dissolved upon imidization to give a deep red solution and the product (V-1) precipitated upon cooling to 165 °C. Complete imidization was confirmed by IR spectroscopy which indicated the loss of the 6-membered anhydride peak at 1774 cm⁻¹ and the appearance of the characteristic imide peak at 1701 and 1667 cm⁻¹. The ¹H NMR spectrum of perylene bisphenol V-1 showed four doublet resonances each with a relative integration of two as a result of the two AB-spin systems present in the A-BPA moiety. The large multiplet representing the two overlaid doublets of the aromatic protons from the perylene moiety was present at 8.98 ppm with a total integration of four. Furthermore, the ¹³C NMR spectrum of V-1 exhibited the 17 nonequivalent carbon resonances as expected. The UV-Vis spectrum of V-1 showed the characteristic tri-modal absorbance at 459, 489 and 524 nm with molar extinction coefficients of 8260, 15600, and 19930 Lmol⁻¹cm⁻¹, respectively. The solubility of perylene bisphenol V-1 improved over the starting PTDA as it became slightly soluble in hot DMAc.

Scheme V.1 Synthesis of perylene bisphenol monomer V-1

The synthesis of naphthalene bisphenol V-2 from NTDA, was achieved in a similar manner using a slight excess of A-BPA and a catalytic amount of zinc acetate in DMAc (Scheme V.2). Again, complete imidization was indicated by IR spectroscopy with the loss of the 6-membered anhydride stretch at 1779 cm^{-1} and the appearance of the characteristic imide peaks at 1709 and 1670 cm^{-1} . The ^1H NMR spectrum showed the same four doublet resonances each with a relative integration of two as in monomer V-1. The large singlet resonance representing the equivalent four aromatic protons of the NTDA moiety was present at 8.89 ppm with a relative integration of two. Furthermore, the ^{13}C NMR spectrum of V-2 exhibited the 14 nonequivalent carbon resonances as expected. The UV-Vis spectrum of V-2 showed two peaks at 359 and 379 nm with molar extinction coefficients of 23110 and $23940\text{ Lmol}^{-1}\text{cm}^{-1}$, respectively. The naphthalene bisphenol V-2 was soluble in most conventional organic solvents.

Scheme V.2 Synthesis of naphthalene bisphenol monomer V-2

V.3 Electrochemistry and Spectroelectrochemistry of Imide-Bisphenols.

Using the standard electrochemical apparatus consisting of a working platinum electrode, a platinum counter electrode and a Ag/Ag^+ reference electrode, the cyclic

voltammograms of monomers V-1 and V-2 were recorded in DMAc using 0.1 M tetra-*n*-butylammonium perchlorate as the supporting electrolyte. Both monomers undergo two reversible one-electron reductions, the first of which is the reduction of the neutral monomer to the radical anion and the second reduction corresponds to the formation of the dianion. The first reduction of perylene bisphenol V-1 to the corresponding radical anion occurred at $E^{\circ}_{1/2} = -0.23$ V vs. NHE, followed by the formation of the corresponding dianion at $E^{\circ}_{1/2} = -0.47$ V vs. NHE (Figure V.7). Similarly, naphthalene

Figure V.7 Cyclic voltammogram of V-1

bisphenol V-2 underwent two one-electron reductions at $E^{\circ}_{1/2} = -0.25$ V and -0.60 V vs. NHE (Figure V.8). The difference in the half wave potentials of the radical anion and the dianion in the two monomers (V-1: 0.24 mV, V-2: 0.35 mV) is due to the extended

conjugation and potential delocalization of the radical anion in the case of monomer V-1.⁹

Figure V.8 Cyclic voltammogram of V-2

Both monomers are electrochromic as evident by the observed spectro-electrochemistry. Upon reduction of perylene bisphenol V-1 from the neutral state to the radical anion, the absorption bands underwent a bathochromic shift from 459, 489 and 524 nm to 702, 796 and 958 nm. Further reduction induces a hypsochromic shift to 570 and 650 nm (Figure V.9a), as characteristics of numerous imide systems reported by Viehbeck et al.³ Similarly, naphthalene bisphenol V-2 had initial peaks in the UV-Vis spectrum at 359 and 379 nm, however upon a one-electron reduction the resulting radical anion had peaks at 473, 605 and 703 nm. Upon further reduction to the dianion state also

results in a hypsochromic shift to 400, 423 and 624 nm (Figure V.9b). Also of interest is the observed increase in the molar extinction coefficient of the fully reduced dianions of

Figure V.9 UV-Vis-NIR spectroelectrochemistry of V-1. (a) neutral, (b) -600 mV and (c) -1000 mV.

V-1 and V-2. The original λ_{max} of V-1 was at 524 nm with an ϵ value of $19930 \text{ Lmol}^{-1} \text{cm}^{-1}$ and upon complete reduction the dianion had a λ_{max} at 570 nm with an ϵ value of $22920 \text{ Lmol}^{-1} \text{cm}^{-1}$. Similarly, the λ_{max} of V-2 in the neutral state was at 379 nm with an ϵ of $23940 \text{ Lmol}^{-1} \text{cm}^{-1}$ and upon reduction to the dianion, had a λ_{max} at 423 nm with an ϵ of $29810 \text{ Lmol}^{-1} \text{cm}^{-1}$.

Figure V.10 UV-Vis-NIR spectroelectrochemistry of V-2 (a) neutral, (b) -600 mV and (c) -1000 mV.

V.4 Polymer Synthesis and Characterization.

Two analogous series of poly(aryl ether imide)s were prepared based on bisphenol monomers V-1 and V-2. The two series of copolymers (V-1 to V-5 and V-6 to V-10) based on perylene bisphenol V-1 were obtained by polycondensation of BPA and either 4-fluorophenyl sulfone or 4,4'-difluorobenzophenone in the presence of cesium carbonate and magnesium hydroxide¹⁰ in DMAc (Scheme V.3). High molecular weight polymers were obtained when the feed ratio of monomer V-1 was kept at 5, 10 and 20%. Upon higher feed ratios, oligomers were formed due to the limited solubility of V-1 under the polymerization conditions used. All the perylene poly(aryl ether imide)s were

purified by reverse precipitation from chloroform/methanol and the content (mol %) of monomer V-1 incorporated in the polymer was determined by UV-Vis spectroscopic methods based on the Beer-Lambert calibration curve of monomer V-1 (Table V.1).

Scheme V.3 Copolymerization of V-1 poly(aryl ether)s

Table V.1 Characterization of perylene diimide containing poly(aryl ether imide)s

PAE	n ^a	Ar ^b	Mol% ^c	T _g (°C) ^d	T _d (°C) ^e	M _w ^f	M _n ^f	M _w /M _n	η _{inh} ^g
V-1	0.05	DFS	2.4	194	495	63500	24700	2.5	0.41
V-2	0.10	DFS	3.9	205	476	69200	26000	2.6	0.44
V-3	0.20	DFS	7.4	220	482	15200	8600	1.8	0.17
V-4	0.35	DFS	10.0	240	449	10100	2700	3.7	0.13
V-5	0.50	DFS	13.1	233	447	6400	3100	2.0	0.11
V-6	0.05	DFK	2.6	153	500	35900	13600	2.6	0.30
V-7	0.10	DFK	4.5	160	496	53600	13500	3.9	0.36
V-8	0.20	DFK	7.3	170	491	14200	6900	2.1	0.16
V-9	0.35	DFK	10.6	225	460	7900	4300	1.9	0.14
V-10	0.50	DFK	11.8	219	444	3700	3700	1.7	0.11

^a mol% ratio of V-1 in monomer feed relative to BPA.^b Derived from DFS = 4-fluorophenyl sulfone, DFK = 4,4'-difluorobenzophenone.^c Mole percent of V-1 incorporated into polymers determined by UV-VIS spectroscopy.^d DSC analysis under N₂ at a heating rate of 10 °C/min, T_g taken from second scan.^e Temperature for 5% weight loss, as assessed by TGA under N₂ at a heating rate of 10 °C/min.^f Measured by GPC relative to polystyrene standards.^g Inherent viscosity in CHCl₃ at 25 ± 0.1 °C (0.5 g/dL).

The preparation of high polymer was initially indicated by the gel permeation chromatography and the fibrous nature of the collected polymers. Copolymers V-1 to V-3 and V-6 to V-8 were fibrous and had acceptable inherent viscosities. Copolymers V-4, V-5, V-9 and V-10 were of low molecular weight as characterized by GPC with average molecular weights (M_w) ranging from 3700 to 10100. The measured glass transition temperatures (T_g) for V-1 to V-4 and V-6 to V-8 resulted in good linear dependence on the mol% content of monomer V-1 over the range of high polymers (Figure V.11).

Figure V.11 T_g versus wt% content of electroactive monomer. (● = V-1 to V-4, ■ = V-6 to V-8)

Poly(aryl ether imide)s V-11 to V-15 and V-16 to V-20 were prepared from naphthalene bisphenol monomer V-2, BPA and either bis(4-fluorophenyl)sulfone or 4,4'-difluorobenzophenone (Scheme V.4). The resulting polymers were characterized and are reported in Table V.2. All polymers derived from monomer V-2 were fibrous after reverse precipitation and had good inherent viscosities, with the exception of V-15 and V-20, which also had low inherent viscosities and average molecular weight. The measured T_g of polymers V-11 to V-15 and V-16 to V-20 resulted in a linear dependence on mol% content of monomer V-2 over the range of high polymers (Figure V.12).

Scheme V.4 Copolymerization of V-2 poly(aryl ether)s

Table V.2. Characterization of naphthalene diimide containing poly(aryl ether imide)s

PAE	n ^a	Ar ^b	Mol% ^c	T _g (°C) ^d	T _d (°C) ^e	M _w ^f	M _n ^f	M _w /M _n	η _{inh} ^g
V-11	0.10	DFS	4.0	208	482	80800	30900	2.6	0.55
V-12	0.20	DFS	8.8	230	483	67900	32900	2.0	0.63
V-13	0.35	DFS	12.0	245	476	28700	7200	3.5	0.41
V-14	0.50	DFS	20.4	254	481	30500	13400	2.2	0.30
V-15	1.00	DFS	29.8	317	452	12200	5300	2.2	0.23
V-16	0.10	DFK	4.8	173	498	93900	22100	4.2	0.66
V-17	0.20	DFK	9.2	183	507	33000	7600	4.3	0.38
V-18	0.35	DFK	17.0	204	495	24200	6500	3.7	0.31
V-19	0.50	DFK	22.0	220	495	17500	7200	2.4	0.25
V-20	1.00	DFK	34.7	258	490	7800	3200	2.5	0.16

^a mol% ratio of V-2 in monomer feed relative to BPA.^b Derived from DFS = 4-fluorophenyl sulfone, DFK = 4,4'-difluorobenzophenone.^c Mole percent of V-2 incorporated into polymers determined by UV-VIS spectroscopy.^d DSC analysis under N₂ at a heating rate of 10 °C/min.^e Temperature for 5% weight loss, as assessed by TGA under N₂ at a heating rate of 10 °C/min.^f Measured by GPC relative to polystyrene standards.^g Inherent viscosity in CHCl₃ at 25 ± 0.1 °C (0.5 g/dL).

Figure V.12 T_g versus mole % content of electroactive monomer V-2.
(▲ = V-11 to V-15, ◆ = V-16 to V-20)

V.5 Electrochemistry and Spectroelectrochemistry of Electrochromic Polymers.

Spectroelectrochemical characterization of poly(aryl ether imide)s, derived from electroactive bisphenols V-1 and V-2, were carried out in the same manner as for the monomers. The electroactivity of poly(aryl ether imide)s derived from monomer V-1 were ascertained through the use of cyclic voltammetry. A dilute solution of polymer V-7 as measured under the same conditions as V-1, however due to its limited solubility in the electrolyte solution, very weak currents were observed. The resulting cyclic

voltammogram of V-7 was overlayed on that of V-1 in Figure V.13, which shows two one-electron reductions with similar half wave potentials. The UV-Vis-NIR spectroelectrochemistry was done in-situ through the use of an Ottle cell. The UV-Vis-NIR spectrum showed the same patterns as observed for monomer V-1 upon reduction to the radical anion and dianion species thus indicating that the same spectroelectrochemistry occurs in poly(aryl ether imide) V-7 as in monomer V-1 (Figure V.14) Therefore, poly(aryl ether imide)s derived from the perylene bisphenol monomer V-1 are also electrochromic.

Figure V.13 Cyclic voltammogram of V-7 (dashed line) compared to V-1

Figure V.14 UV-Vis-NIR spectroelectrochemistry of V-7. (a) neutral, (b) –600 mV and (c) –1000 mV.

The electroactivity of V11 to V-15 and V-16 to V-20 derived from monomer V-2 was determined by cyclic voltammetry and in-situ spectroelectrochemistry. The cyclic voltammogram of V-20 showed two one-electron reductions similar to monomer V-2, however were slightly shifted to more negative potentials (Figure V.15). Spectroelectrochemistry is referenced only to Ag/Ag^+ and is uncorrected to the standard ferrocene redox couple as previously done for the monomers. The in-situ spectroelectrochemistry showed the same red shift for of the radical anion, followed by a blue shift corresponding to the formation of the dianion species similarly to that of monomer V-2. Based on the solution electrochemistry and in-situ UV-Vis-NIR

spectroelectrochemistry, poly(aryl ether imide)s derived from naphthalene bisphenol monomer V-2 were also shown to be electrochromic (Figure V.16).

Figure V.15 Cyclic voltammogram of V-20 (dashed line) compared to monomer V-2

Figure V.16 UV-Vis-NIR spectroelectrochemistry of V-20 (a) neutral, (b) -600 mV and (c) -1000 mV.

V.6 Investigations into Solid State Electrochromic Display Devices.

In order to transfer the electrochromic behavior observed in solution, to an all solid state electrochromic devices, a solid-state half-cell was first tested. Through the use of an Ottle cell, as previously employed with solution electrochemistry, solid-state half cells were constructed using the same solution electrolytes (Figure V.17).

Figure V.17 Schematic representation of a solid state half cell in an Ottle cell.

The electrochromic polymer V-5 was spin-coated from 5 wt % solution in 1:1 chloroform:tetrachloroethane onto etched ITO surfaces and dried under vacuum for 1 hr at 100 °C. The half cells were constructed in the same manner as the solution spectroelectrochemistry behavior was determined. Monitoring of the percent transmission at 575 nm while cycling the applied voltage between +0.2 V (bleached) to – 1.0 V (colored) showed an initial $\Delta\%T$ of ~21 %. The steady decrease in $\Delta\%T$ indicates a possible short lifetime, however upon inspection of the half cell, the polymer appeared to have increased solubility in the electrolyte when in the n-doped colored state (Figure V.18).

Figure V.18 Ottle cell half cell construction of polymer V-5 monitoring %T at 575 nm during a voltage switch from +0.2 V to -1.0 V

The appearance of soluble electrochromic polymers in the n-doped state may lead to enhanced switching speeds in the solid state cell if the polymer does not diffuse into the electrolyte. In a solid state cell, theoretically there is a very minute amount of solvent originating from the polymer gel electrolyte, which may greatly reduce the solvating power and allow for longer lifetimes. In order to investigate the potential use of electrochromic polymers in all solid state devices, a suitable counter electrode needs to be chosen that has a similar voltage requirement for the redox chemistry to take place. The choice of poly(3-hexyl thiophene) (P3HT) is complimentary to the bleached and colored states of polymer V-5. In the neutral state P3HT is orange and polymer V-5 red, where

upon application of a voltage in the forward bias, P3HT turns blue and polymer V-5 becomes purple. The solid state devices were constructed by initially spin coating both P3HT (1 wt%) and V-5 (5 wt%) solutions (1:1 CHCl₃:TCE) on separate ITO slides (1 cm x 7.5 cm). The films were then dried at 100 °C for 2 hrs and electrolyte was then applied to one of the slides and the second was placed on top limiting the amount of air bubbles. The construction was done in a glove bag under a nitrogen atmosphere and allowed to dry in the glove bag for 48 hrs. The sandwich cell devices were then dried under high vacuum for 24 hrs at 100 °C and the spectroelectrochemistry was measured in the same fashion as before. The monitoring of percent transmission at 650 nm was chosen as both electrochromic materials have an absorbency that coincide. The applied voltage was cycled between +2.5 V and -2.5 V and the 1st switch gave an initial $\Delta\%T$ of 16.1 % and the 1000th switch retained 62 % of the original with a $\Delta\%T$ of 10 % (Figure V.19)

Figure V.19 Lifetime study of all solid-state ECD sandwich cell monitoring %T at 650 nm for a voltage switch between +2.5 V and -2.5 V at 650 nm (a) 1st switch (b) 1000th switch

V.7 Conclusions

This work has demonstrated the successful incorporation of rigid electrochromic perylene diimide and naphthalene diimide units into poly(aryl ether imides) through the polycondensation of bisphenols V-1 and V-2 with activated dihalides. The resulting soluble poly(aryl ether imide)s were shown to be electroactive and electrochromic in both solution and the solid state. The solubility of the polymer V-5 in the electrolyte when doped is most probably the result of low lifetime of the electrochromic device.

V.8 Experimental Section

Materials. 1,4,5,8-Naphthalenetetracarboxylic dianhydride, N,N-dimethylacetamide (DMAc), 1-methyl-2-pyrrolidinone (NMP), chlorobenzene, zinc acetate, cesium carbonate and magnesium hydroxide were purchased from Aldrich Chemical Company and used as received. 3,4,9,10-Perylenetetracarboxylic dianhydride was purchased from Aldrich and purified as reported.⁶ 2-(4-Aminophenyl)-2-(4-hydroxyphenyl) propane (A-BPA) was prepared as reported in the literature.⁸ Bisphenol A (BPA) was purchased from Aldrich and recrystallized from toluene prior to use. Monomer grade 4-fluorophenyl sulfone and 4,4'-difluorobenzophenone were purchased from Marshallton (Winston-Salem, NC) and (Oakwood Products Inc., SC) respectively and used as received. Spectrophotometric grade DMAc, ferrocene and tetrabutylammonium perchlorate were purchased from Aldrich and used for the electrochemical characterization of monomers and polymers.

Measurements.

The monomers and polymers were measured as outlined in Chapter Two with the following exceptions. BAS 100W electrochemical station was used to obtain all $E^{\circ}_{1/2}$ via cyclic voltammograms calibrated to Fe(II)/Fe(III)^+ oxidative couple. The spectroelectrochemical measurements were done in an Ottle Cell, using 10 Ω indium-tin-oxide (ITO) coated glass slides (Delta Technologies).

Preparation of Perylene Bisphenol V-1.

In a 500 mL, 3-necked, round-bottomed flask fitted with an Ar inlet/outlet and a Dean-Stark trap, PTDA (10.0 g, 25.5 mmol), A-BPA (28.9 g, 127.1 mmol) and $\text{Zn}(\text{OAc})_2$ (0.60 g, 3.30 mmol) were suspended in NMP (100 mL) and heated to reflux. After 1 h, IR showed no starting material and the suspension was cooled to 150 °C and filtered through a 150 mL medium-porosity sintered glass filter. The dark red solids were washed successively with boiling DMF (2 x 50 mL), and methanol (3 x 50 mL). The resulting product was dried at 60 °C under vacuum (5 mm Hg) for 16 h. Yield 17.4 g (82 %); m.p. >300 °C; ^1H NMR [400 MHz, CDCl_3/TFA (4:1)] δ 8.89 (m, 4H), 7.46 (d, 2H), 7.26 (d, 2H), 7.22 (d, 2H), 6.86 (d, 2H), 1.72 (s, 6H); ^{13}C NMR [100 MHz, CDCl_3/TFA (4:1)] δ 166.12, 154.07, 152.25, 144.51, 136.53, 134.05, 131.62, 130.43, 129.29, 129.00, 128.38, 127.15, 125.07, 123.25, 115.79, 43.37, 31.33; IR (KBr) 1701 and 1667 cm^{-1} (C=O, imide); MS (FAB, m/e , relative intensity %) 811 (M^+ , 1.0).

Preparation of Naphthalene Bisphenol V-2.

In a 500 mL, 3-necked, round-bottomed flask fitted with an Ar inlet/outlet and a Dean-Stark trap, NTDA (5.6 g, 20.9 mmol), A-BPA (10.0 g, 44.0 mmol) and $\text{Zn}(\text{OAc})_2$ (0.39 g, 21.3 mmol) were suspended in DMAc (100 mL) and heated to reflux. After 3 hours IR showed no starting material and the solution was precipitated into 1 L of methanol. The precipitate was collected on a sintered glass filter funnel and washed with methanol (3 x 50 mL). The resulting orange-brown solid was dried at 60 °C under vacuum (5 mm Hg) for 16 h. Yield 13.1 g (91 %); m.p. >300 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.98 (s, 2H), 7.49 (d, 2H), 7.28 (d, 2H), 7.23 (d, 2H), 6.86 (d, 2H), 1.75 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.58, 153.65, 151.15, 143.88, 132.70, 130.41, 128.62, 128.24, 127.72, 127.45, 126.75, 114.18, 42.60, 30.40; IR (KBr) 1709 and 1670 cm^{-1} (C=O, imide); MS (FAB, m/e , relative intensity %) 687 (M^+ , 4.8).

Typical Polymerization.

BPA (0.5066 g, 2.220 mmol), 4-fluorophenyl sulfone (0.6269 g, 2.470 mmol), V-1 (0.2000 g, 0.250 mmol), Cs_2CO_3 (0.844 g, 2.590 mmol) and $\text{Mg}(\text{OH})_2$ (0.151 g, 2.590 mmol) were placed in a 25 mL, 3-necked, round-bottomed flask equipped with a

magnetic stirrer, Ar inlet/outlet, condenser and Dean-Stark trap. The soluble components were dissolved in DMAc (6.5 mL) and toluene (6.5 mL). The reaction flask was purged with Ar for 30 min and at which time the red mixture was heated to 160 °C (oil bath temperature). The reaction temperature was maintained and the solution turned a dark purple color after about 2 h. Polymerization was monitored by GPC and terminated when the molecular weight failed to increase. The polymerization solution was cooled and diluted with DMAc (10 mL) and precipitated into methanol (300 mL). The resulting polymer was filtered, redissolved in chloroform (30 mL) and filtered through a pad of Celite to remove inorganic salts. High molecular weight polymer was obtained by reverse precipitation through the slow addition of methanol (20–40 mL) to the filtrate. The obtained fraction was again dissolved into a minimum of chloroform and precipitated into methanol. The resulting polymer V-2 was dried at 100 °C under vacuum (5 mm Hg) for 24 h.

Cyclic Voltammetry and In-situ Electrochemistry – UV-Vis-NIR Spectroscopy.

Cyclic voltammetry (CV) experiments of V-1 and V-2 were carried out in a three-electrode cell consisting of a platinum working electrode, a platinum counter electrode and a Ag/Ag⁺ reference electrode, at a sweep rate of 200 mV/s. Millimolar solutions of the monomers were prepared in spectrophotometric grade DMAc dried over 4Å molecular sieves. The supporting electrolyte was 0.1 M tetra-*n*-butylammonium perchlorate dried overnight at 100 °C. The solutions were deoxygenated by sparging

with Ar for 15 min prior to scanning and blanketed with argon during scans. All CVs are corrected to the Fe(II)/Fe(III)^+ oxidative couple of 0.72 mV vs. NHE in DMF.

In-situ spectroelectrochemical measurements were accomplished through the use of an Ottle cell consisting of an ITO coated glass surface as the working electrode, a platinum counter electrode and a Ag/Ag^+ reference electrode. The UV-Vis-NIR spectrum was monitored over the complete reduction of electroactive species. The solutions of monomers V-1 and V-2 used for the CV experiments were used for the in-situ spectroelectrochemistry experiments and polymer solutions were obtained by saturating supporting electrolyte with the appropriate polymer. Each UV-Vis-NIR spectrum was obtained after holding the specified applied potential for 60 s and was maintained throughout the entire measurement.

V.9 References

- 1) Granquist, C. G. in *The CRC Handbook of Solid State Electrochemistry*. Gellings, P. G.; Bouwmeester, H. J. M. Eds.; CRC Press Inc: New York, 1996; p 587.
- 2) Sapp, S.; Sotzing, G. A.; Reynolds, J. R. *Chem. Mater.* **1998**, *10*, 2101.
- 3) (a) Mazur, S.; Lugg, P. S.; Yarnitzky, C. *J. Electrochem. Soc.; Electrochem. Sci. and Techn.* **1987**, *134*, 346. (b) Krause, L. J.; Bales, J. L. *J. Electrochem. Soc.; Electrochem. Sci. and Techn.* **1988**, *135*, 1137. (c) Viehbeck, A.; Goldberg, M. J.; Kovac, C. A. *J. Electrochem. Soc.; Electrochem. Sci. and Techn.* **1990**, *137*, 1460.
- 4) Horowitz, G.; Kouki, F.; Spearman, P.; Fichon, D.; Nogues, C.; Pan, X.; Garnier, F.; *Adv. Mater.* **1996**, *8*, 242.
- 5) Posch, P.; Thelakkat, M.; Schmidt, H. W. *Syn. Metal.* **1999**, *102*, 1110.
- 6) (a) Wang, Z. Y.; Qi, Y.; Gao, J. P.; Sacripante, G. G.; Sundararajan, P. R.; Duff, J. D. *Macromolecules* **1998**, *31*, 2075. (b) Lu, W.; Gao, J. P.; Wang, Z. Y.; Qi, Y.; Sacripante, G. G.; Sundararajan, P. R.; Duff, J. D., *Macromolecules*, **1999**, *32*, 8880.
- 7) Williams, M. E.; Murray, R. W. *Chem. Mater.* **1998**, *10*, 36033.
- 8) Jurek, M. J.; McGrath, J. E., *Polymer* **1989**, *30*(8), 1552.
- 9) Lee, S. K.; Zu, Y.; Herrmann, A.; Geerts, Y.; Müllen, K.; Bard, A. J. *J. Am. Chem. Soc.* **1999**, *121*, 3513.
- 10) Martinez, C. A.; Hay, A. S.; *J. Polym. Sci. Part A: Polym. Chem.* **1997**, *35*, 2015.

Contributions to Knowledge

- 1. Increases in T_g of poly(aryl ether sulfone)s derived from tetrahydro[5]helicene subunits result from contributions from both the rigid helical nature of the *o*-terphenyl as well as the inherent structure, as determined through the incorporation of the analogous non-bridged *o*-terphenyl subunit.**
- 2. Macrocyclic formation is facilitated in non-bridged *o*-terphenyl units owing the greater degree of rotational freedom, evident by the observed chain growth and concurrent cyclodepolymerization.**
- 3. Photopatternable poly(aryl ether imide)s may be prepared through the introduction of cinnamate moieties via hydroxy-containing poly(aryl ether imide)s derived from A_2X -type diamino naphthalimide monomer.**
- 4. Poly(aryl ether)s derived from perylene and naphthalene imide-bisphenol monomers are found to be electrochromic and cathodically-coloring in solution and in the solid-state as a thin film.**