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**DESIGN, SYNTHESIS AND CHARACTERIZATION OF NAPHTHALENE-
BASED POLY(ARYL ETHER)S**

by

Judy E. Douglas, 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, ON Canada

March 1998

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JUDY DOUGLAS, B.Sc

in partial fulfillment of the requirements
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ABSTRACT

Modifications to poly(aryl ether)s (PAE) are carried out by making structural changes on a molecular level (i.e. monomers) with the aim of attaining novel properties on a macroscopic level (i.e. with the polymer). Traditionally, these changes have been made on the bisphenol portion of PAE. This thesis focuses on the design and synthesis of several new dihaloaryl monomers. The designs are rationalized based on predicted structure-property relationships which are investigated.

A 1,4-naphthylene moiety is incorporated into both ketone and sulfone activated dihaloaryl monomers which are polymerized to obtain two new series of poly(aryl ether sulfone)s (PAES) and poly(aryl ether ketone)s (PAEK). The PAES and PAEK displayed glass transition temperatures in the range of 218 to 317 °C and 188 to 290 °C, respectively. Degradation temperatures for 5% weight loss in nitrogen occurred above 390 °C for the PAES and 440 °C for the PAEK. In both series, 1,4-naphthylene insertion serves to increase glass transition temperature, reduce crystallinity, improve gas permselectivity while lowering gas permeability.

An axial chiral element, i.e. *ortho* substituted 1,1'-binaphthyl, was incorporated into a ketone activated dihaloaryl monomer. Glass transition temperatures of the resulting PAEK ranged from 225 to 287 °C depending on the bisphenol used. Degradation temperatures for 5% weight loss in nitrogen occurred above 485 °C. The binaphthalene-based polymer was subjected to a transformation reaction, which led to incorporation of a chiral [5]helicene moiety into the PAE displaying a T_g of 265 °C and T_d of 459 °C.

Therefore, a new route to the introduction of axial and helical chirality into PAE was demonstrated. Despite failed attempts to chemically resolve the racemic binaphthyl monomer, chiral chromatography was successful in separating the binaphthyl monomer into its two enantiomeric forms thus paving a route to optically active [5]helicene-based PAE.

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SYMBOLS AND ABBREVIATIONS

Polymer Terminology

PAE	Poly(aryl ether)
PAEK	Poly(aryl ether ketone)
PAES	Poly(aryl ether sulfone)
PEEK	Poly(ether ether ketone)
S_NAr	Aromatic nucleophilic substitution
M_w	Weight-average molecular weight
M_n	Number-average molecular weight
P	Permeability (Barrers)
α	Selectivity toward a pair of gases
T_g	Glass transition temperature
T_m	Crystalline melting temperature
E'	Young's modulus
T_d	Onset decomposition temperature for 5% weight loss
δ	Chemical shift (ppm)
η_{inh}	Inherent viscosity

Solvents

DMAc	N,N-Dimethylacetamide
DMF	N,N-Dimethylformamide
NMP	N-Methyl-2-pyrrolidinone
PhCl	Chlorobenzene

TMSO₂	Tetramethylene sulfone
TCE	1,1,2,2-Tetrachloroethane
THF	Tetrahydrofuran

Bisphenols

BPA	Bisphenol A or 4,4'-(Isopropylidene)diphenol
BPS	Bis(4-hydroxyphenyl)sulfone
BP	4,4'-Biphenol
6F-BPA	4,4'-(Hexafluoroisopropylidene)diphenol
HFP	9,9-Bis(4-hydroxyphenyl)fluorene
HQ	1,4-Hydroquinone
PP	Phenolphthalein
PZ	1,2-Dihydro-4-(4-hydroxyphenyl)(2H)phthalazin-1-one
TMBP	2,2',6,6'-Tetramethyl-4,4'-biphenol

Characterization

COSY	Correlated spectroscopy
DSC	Differential scanning calorimetry
GPC	Gel permeation chromatography
HETCOR	Heteronuclear shift correlation
HPLC	High performance liquid chromatography
IR	Infrared
J	Coupling constant
mp	Melting point

MS	Mass spectrometry
NMR	Nuclear magnetic resonance
TGA	Thermogravimetric analysis
TLC	Thin layer chromatography
TMA	Thermomechanical analysis
UV/VIS	Ultra-violet/visible

L1. Poly(aryl ether)s

The term 'engineering plastic' refers to a family of polymers which exhibit superior mechanical and thermal stability.¹ Engineering plastics are made on a smaller scale and at greater cost than commodity plastics whose mechanical properties are typically compromised below 100 °C. Examples of engineering plastics include: polyamides (nylons), polyimides, polyesters, polycarbonates and polysulfides.¹

An important group of polymers that fall within the 'engineering plastics' category are the poly(aryl ether)s (PAE).²⁻⁸ They include poly(aryl ether imide)s, poly(phenylene ether)s, poly(aryl ether ketone)s and poly(aryl ether sulfone)s. As with the other aromatic polymers, they possess a high degree of thermal stability⁶ and are known for their superior performance characteristics in a number of application areas.¹⁻⁸

Crucial to the commercial success of the poly(aryl ether)s is their ability to be processed which is possible due to the presence of the ether link. Without it, the polymers would have glass transition temperatures (T_g) which are too high or unmeasurable and thus remain too inflexible to be soluble or melt processed (Figure I.1).²

Glass transition temperature (T_g) is one of the most important characteristics by which a polymer is assessed and is characteristic of the amorphous state. Amorphous polymers lack regions of order. Crystalline polymers contain ordered domains interconnected by amorphous regions. When heated, a polymer with an amorphous region will soften over a broad range losing its glass-like properties to assume a more rubber-like character and this occurs at the glass transition temperatures or ' T_g '. On a molecular level, T_g is accompanied with greater segmental motion of the polymer chains, greater rotational

freedom and an increase in free volume (the space between the polymer chains). On a macroscopic level, a change in enthalpy occurs which is measured by differential scanning calorimetry (DSC). Likewise, a decrease in chain stiffness, or modulus, is observed at T_g which is detected by mechanical measurements. When a crystalline polymer is heated, the ordered regions melt over a narrow range and this is referred to as the crystalline melting point or T_m . In general, glass transition temperatures are usually about one half to two thirds the temperature of crystalline melting points in degrees Kelvin.⁶

Generally, the stiffer the polymer, the higher the T_g . For high-temperature applications, the higher the T_g , the more useful it is. Structural features which restrict the polymer's chain mobility will increase the T_g . Figure I.1 shows how varying the ratio of ether to ketone or sulfone can in fact lower the T_g of several poly(aryl ether)s.

Figure I.1. Effect of ether linkage on T_g of poly(arylene)s²

One of the most successful poly(aryl ether)s made to date is the poly(aryl ether imide) UltemTM shown in Figure I.2 which was introduced by the General Electric Company in 1982.² Applications of this polyimide include microelectronics, jet engine parts and aerospace industry.

Figure I.2. Poly(aryl ether imide)

I.1.1. Poly(aryl ether ketone)s

Poly(aryl ether ketone)s, or PAEK, make up an important class of poly(aryl ether)s.⁹ The ketone group is trigonal planar (Figure I.3) which facilitates chain packing and can sometimes lead PAEK to display crystalline behaviour. Poly(aryl ether ketone)s are typically strong rigid materials with outstanding heat resistance. They possess excellent electrical insulating properties, low flammability and high chemical resistance. They can be injection moulded and extruded and can be processed into fibers, films or coatings. Applications of poly(aryl ether ketone)s include coatings for high performance wiring in aeronautics and advanced structural composites.

An important commercial example is poly(ether ether ketone), or PEEK, whose structure is shown in Figure I.3.^{10,11} PEEK has a T_g of 143 °C and T_m of 334°C.¹²

Figure I.3. PEEKTM

I.1.2. Poly(aryl ether sulfone)s

Another important family of poly(aryl ether)s are the poly(aryl ether sulfone)s or PAES.¹³ The sulfone group is polar and tetrahedral. Polymers containing this group exhibit higher degrees of chain stiffness, high glass transition temperatures (T_g) and are usually amorphous.

PAES also possess excellent oxidative and environmental stability, superior physical properties, good flame, hydrolytic, electrical and solvent resistance. They can be found in a variety of forms such as molded parts, fibers and coatings.¹³ Poly(aryl ether sulfone)s are used as car engine parts, hot water fittings, sterilizable medical equipment, electrical components and household molded products.^{13b} Three commercially successful polysulfones are Udel™, Radel™ and Victrex™ (Figure I.4). Udel™ has received a lot of interest in recent years due to its favorable gas transport properties and will be discussed further in Section I.4.¹³

Figure I.4. Structures of commercial polysulfones

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

There are several synthetic routes to poly(aryl ether)s. These include aromatic electrophilic substitution, aromatic nucleophilic substitution, metal coupling and ring-opening polymerizations.² The most widely used method, both in industry and research laboratories, is the nucleophilic displacement of bisphenoxides with activated dihaloaryl monomers.^{2,14} This approach, in addition to others, is discussed in further detail.

I.2.1. Aromatic Electrophilic Substitution

Poly(aryl ether)s were first made in industry by aromatic electrophilic substitution. This approach involves the electrophilic attack of an electron deficient species on an aromatic ring and is often referred to as Friedel-Craft polyacylation.^{15,16} The electron deficient species can be a sulfonylium ($-\text{SO}_2^+$) or acylium ($-\text{CO}^+$) ion. These ions are generally derived from corresponding acyl chlorides or sulfonyl chlorides. Aromatic rings, often activated by an ether group in the para position, will react with the above species in the presence of Lewis acids such as AlCl_3 or BF_3 in solvents such as carbon disulfide, dichloromethane or nitrobenzene. Disadvantages of this approach include branching due to acylation in the ortho position, the use of relatively expensive toxic reagents and the limited number of monomers available.¹⁵

Figure I.5 illustrates two commercial products: StilanTM and AstrelTM 360 which were made by aromatic electrophilic substitution.¹⁵ StilanTM was first introduced by the Raychem Corporation in the early 1970's and was produced by the electrophilic polymerization of *p*-phenoxybenzoyl chloride in liquid HF, catalyzed by BF_3 . Difficulties of handling HF on a large scale led to the discontinuance of this product made by this

route. The 3M Company introduced Astrel™ 360, a copolymer, in 1967 using FeCl_3 , a Lewis acid catalyst, in small amounts. Yet, it was discontinued in 1976 because of difficulties in melt fabricating the polymer and the ready availability of other polysulfones prepared by nucleophilic displacement polymerization.

Figure I.5. Aromatic electrophilic substitution³

I.2.2. Nucleophilic Aromatic Substitution

Farnham and Johnson's research led to the development of the successful nucleophilic route to poly(aryl ether)s.¹⁷ The polycondensation requires the presence of an 'activated' dihalo monomer and bisphenol. The term 'activated' refers to the presence of an electron withdrawing group, usually in the para position to the halide. Scheme I.1 shows the general requirements needed for aromatic nucleophilic substitution to occur.

Scheme I.1. General aromatic nucleophilic substitution¹⁷

I.2.2a. Mechanisms of Aromatic Nucleophilic Substitution

There are four principal mechanisms for which aromatic nucleophilic substitution can occur: the benzyne mechanism, S_N1 , $S_{RN}1$ and S_NAr mechanisms.¹⁸

The benzyne mechanism occurs in cases where in the absence of electron withdrawing groups, stronger bases are used (Figure I.6). The first step involves the elimination of the leaving group, followed by attack by the nucleophile not necessarily to the vacant position.

Figure I.6. Benzyne mechanism¹⁸

The S_N1 mechanism usually involves the loss of nitrogen, from a diazonium salt, forming an aryl cation intermediate (Figure I.7). It is then followed by nucleophilic attack.

Figure I.7. S_N1 mechanism¹⁸

The $S_{RN}1$ mechanism is a free radical mechanism which does not require the presence of an electron withdrawing group or strong bases. An electron donor is needed to generate a radical aryl anion which is then attacked by the nucleophile leading eventually to the final species as depicted in the following equations.

It is generally believed that polymerization of bisphenoxides with activated dihaloaryl ketones proceeds through a $\text{S}_{\text{N}}\text{Ar}$ mechanism.^{2,14} The first step involves attack of the aryl halide by the nucleophile to form an intermediate Meisenheimer complex which is stabilized by the presence of an electron withdrawing group (Figure I.8). It is quickly followed by the loss of the leaving group.¹⁸

Figure I.8. Two resonance structures of intermediate Meisenheimer complex

The resonance stabilization of the Meisenheimer intermediate offers a lower activation energy for halogen displacement.¹⁸ The more stabilized the Meisenheimer complex, the more reactive the monomer is. For many known monomers containing 4-halophenyl end groups (e.g., 4,4'-dihalobenzophenone), the Meisenheimer intermediate has two principal resonance structures (Figure I.8). Any benzenoid structure which imparts further resonance stability to the Meisenheimer complex will enhance the reactivity of the monomer in aromatic nucleophilic polymerization.

I.1.2b Factors Governing Aromatic Nucleophilic Polymerization

There are several factors which govern the success of aromatic nucleophilic substitution reactions.¹⁹ Firstly, being a polycondensation reaction, the stoichiometry of the reactants is crucial to the attainment of high molecular weight.

Electron withdrawing groups can vary from simple ketones and sulfones to heteroatom cyclics like quinoxalines²⁰, triazoles²¹ and benzimidazoles²² to name a few. Key to the success of these activating groups is their ability to withdraw the electron and stabilize the Meisenheimer complex through resonance to an electronegative atom by the presence of a site of unsaturation.

It is well known that the rates of S_NAr reactions are greater for activated aryl difluorides than their chloride analogues.¹⁸ This is due to fluorine's large electronegativity which increases the net charge density on the carbon to which it is attached. Consequently, the displacement of fluorine from activated monomers is favored over other halides. In fact, Victrex PEEKTM²³ is made by step-growth polymerization of 1,4-hydroquinone (HQ) with 4,4'-difluorobenzophenone instead of with less expensive 4,4'-dichlorobenzophenone (Figure I.9).²⁴

Figure I.9. Nucleophilic displacement to make PEEKTM¹⁹

In general, the displacement of chlorine from dichloroaryl ketones with bisphenoxides to form high molecular weight PAEK is difficult whereas the displacement of chlorine from dichloroaryl sulfones is facile. However, it has been shown that relatively high molecular weight polymers can be obtained with 4,4'-dichlorobenzophenone and 4,4'-isopropylidenediphenol.²⁵ Exceptions for the ketone series also include the use of (a) a diketo monomer having a 1:1 ketone/chlorine ratio as opposed to one with a 1:2

ketone/chlorine ratio,²⁶ (b) a small amount of potassium fluoride in the presence of a phase transfer catalyst,²⁷ (c) 'reactive' bisphenols, e.g. 9,9-bis(4-hydroxyphenyl)fluorene (HPF)^{26a} and 2,2'-bis(4-hydroxyphenoxy)biphenyl,^{26b} or (d) 'reactive' dichloroheteroarylketones such as bis(5-chlorothieryl-2)ketone.²⁸ 4,4'-Dichlorodiphenyl sulfone is the "workhorse" in the poly(aryl ether sulfone) field and is used in the commercial production of a variety of polysulfones such as UDEL™ (Figure I.10).¹⁹

Figure I.10. Nucleophilic displacement to make UDEL™¹⁹

A base is required to form the bisphenoxide *in-situ* which can then react as a nucleophile to displace the halogen. In the early years, NaOH was used, but was soon replaced by weaker bases (alkali metal carbonates) to avoid hydrolytic side reactions. Coined the "carbonate process", this method was found to be successful in forming high molecular weight polymers.¹⁹ The softer the alkali metal counter ions are, the higher the nucleophilicity of the phenolate and therefore the more reactive it is. Industrially, K₂CO₃ and Na₂CO₃ are most often used, but the more expensive Cs₂CO₃ has been used in laboratories when increased reactivity is required. Disadvantages of the carbonate process include salt contamination and the generation of CO₂ and water which can lead to foaming and production of low molecular weight polymer. To circumvent the former, washing (usually more than 10 times) with water is needed. In the latter case, an azeotroping agent,

like chlorobenzene or toluene, is added in order to remove the water formed in the reaction.

Dipolar aprotic solvents are used since they effectively dissolve the monomers and solvate the polar intermediates formed. N-methyl pyrrolidone (NMP), N,N-dimethylacetamide (DMAc), N,N'-dimethylpropyleneurea (DMPU), N-cyclohexylpyrrolidone (CHP) and tetramethylsulfone (TMSO₂) are but a few choices. When choosing a solvent, it is important to consider its boiling point and if the polymer formed can stay in solution within this temperature range.¹⁹

Side reactions which can lead to lower molecular weight include ether cleavage by fluoride (i.e. KF) or phenoxide ions³⁰ and reductive dehalogenation.³¹ Purification of solvents is necessary in order to minimize these side reactions.

I.2.3. Metal-Catalyzed Coupling Polymerization

Polymerization involving the formation of a carbon-carbon bond via metal-catalyzed coupling has received much attention in recent years.³² This is because of its success in making biaryls in quantitative yields and expectations that it could lead to the synthesis of uniquely structured polymers previously unattainable using existing methods. Two metals which have been studied extensively are nickel and palladium.

I.2.3a Nickel(0)-Catalyzed Coupling Polymerization

Nickel(0)-catalyzed coupling was originally discovered by Semmelhack and co-workers.³³ Modifications by Kende,³⁴ Kumada³⁵ and Colon³⁶ led to the development of a practical method to form biaryls. Conditions require inert atmosphere, the use of an aprotic solvent, like DMAc, catalytic amounts of nickel(0), triphenylphosphine as a ligand

and zinc metal. Zero valent nickel is generated *in-situ* by the reduction of simple nickel salts, like NiBr_2 , with excess zinc dust. Moderate temperatures for polymerization are used ($\sim 80^\circ\text{C}$). Aryl chlorides are generally more available and less expensive than aryl bromides and aryl iodides. Side reactions, such as reductive dehalogenation occur less for aryl chlorides and are limited by the use of mild, dry conditions and catalysts such as 2,2'-bipyridine.

Figure I.11. shows the $\text{Ni}(0)$ -coupling polymerization of a dichloro arylsulfone monomer to give a polysulfone.³⁷ In addition, it is possible to couple aryl chlorides containing other functional groups (e.g. ketones, esters, amides, imides).³⁸ This can offer alternative routes to traditional poly(aryl ether)s or allow access to previously unattainable unique polymers.

Figure I.11. Nickel-coupling polymerization³⁷

I.2.3b Palladium Catalyzed Polymerization

Palladium-catalyzed cross-coupling of bifunctional tin reagents with dihalides yield moderate molecular weight poly(aryl ether ketone)s and poly(aryl ether sulfone)s.³² Figure I.12 illustrates the Pd-catalyzed cross-coupling of 4,4'-dibromobenzophenone with 4,4'-bis(tri-*n*-butylstannyl)diphenyl ether.³⁹

Figure I.12. Pd-catalyzed polymerization³⁹

I.2.4. Ring-Opening Polymerization

The preparation of high molecular weight polymers by ring-opening of cyclic aryl ethers has been pursued recently as a viable alternative to more established methods.⁴⁰ Advantages of this method are: (i) macrocycles can be processed at much lower temperatures than their corresponding higher molecular linear polymers due to their lower melt viscosities and (ii) ring-opening polymerization does not liberate side products as is the case with traditional polycondensation reactions. Cyclics are typically made under high dilution conditions and can be ring-opened with a nucleophilic initiator such as potassium carbonate, cesium fluoride or alkali phenoxides. Figure I.13 shows an example of macrocycle formation followed by ring-opening polymerization to form a high molecular weight poly(aryl ether ketone).⁴¹ Ring-opening polymerization can also be used to make poly(aryl ether sulfone)s.⁴²

Figure I.13. Ring-opening polymerization⁴¹

L3. Modifications to Poly(aryl ether)s

Modifications to poly(aryl ether)s are carried out by making structural changes to the repeat unit which result in variations in the polymer's bulk properties. Chemists have pursued this endeavour for decades in an effort to better understand the structure-function relationship of poly(aryl ether)s in order to control their properties for a variety of applications.

In aromatic nucleophilic polymerization, the constituent monomers are a bisphenol and an activated dihalide aryl. Traditionally, most changes to poly(arylene ether)s have focused on the bisphenol portion of the polymer. Common strategies used to effect desired changes in properties are briefly discussed, followed by specific examples.

In general, the introduction of alkyl groups into polymers usually increases their solubility. The addition of pendant groups usually serves to restrict the rotational freedom of polymer chains, which lead to increases in T_g .

The attachment of pendant groups is also a common strategy used when designing polymer membranes for gas separation.⁴³⁻⁴⁵ Pendant groups increase the interchain spacing (free volume) of a polymer which allow a greater flux of gas molecules and therefore enhanced permeability (P). Yet, structural features which increase a polymer's permeability will often reduce its selectivity (α). Selectivity is the polymer's ability to discriminate between different gas molecules. A general goal of membrane scientists is to increase both the permeability and selectivity of a polymer. Thus a compromise must be met between the structural features which favor one but not the other.

1.3.1. Structural Modifications of Bisphenols

PAEK have high heat resistance and are often semi-crystalline, which gives rise to excellent mechanical strength but poor solubility. The modification of PEEKTM and other poly(aryl ether ketone)s to afford more soluble, higher T_g polymers is well documented.⁴⁶⁻

⁴⁹ Alkyl substitution to the bisphenol part of PEEKTM (1,4-hydroquinone) results in polymers with increased solubility and higher T_g (Figure I.14).^{48,49} Whereas PEEKTM cannot be dissolved in chloroform, the alkyl substituted derivatives can. The addition of polar groups (i.e. carboxylic acid) also leads to further increases to T_g than the alkyl substituents due to increased interchain interaction via hydrogen bonding. Esterification of the acid removes the presence of the intermolecular hydrogen bonds and T_g decreases accordingly.

R	$T_g(^{\circ}\text{C})$
H	144
CH ₃	150
C(CH ₃) ₃	176
CHBr ₂	169
CHO	175
COOH	210
COOMe	157

Figure I.14. Effect of pendant groups on T_g in PEEK^{48,49}

Gas transport properties of poly(aryl ether ketone)s have not been studied as extensively as polyimides and polysulfones. The presence of crystalline domains in polymers like PEEKTM decrease the free volume which limit the flux of gas molecules resulting in low permeabilities. Table I.1 shows glass transition temperatures, permeabilities and separation factors of PEEKTM and alkyl substituted PEEKTM.⁴⁹ As

expected, PEEKTM itself gives rise to some of the lowest permeabilities found in the literature for poly(aryl ether)s. Yet, substitution with tertiary butyl leads to four and five-fold increases in permeability. The use of 2,2',6,6'-tetramethyl-4,4'-biphenol (TMBP) as the bisphenol results in larger increases in permeability towards oxygen and carbon dioxide (18 and 20 times the permeability of PEEK). However, this is accompanied with 25% loss in the O₂/N₂ separation factor and larger losses in the CO₂/CH₄ selectivity. The glass transition temperature of the TMBP-based polyketone ($T_g = 240$ °C) is also much higher than PEEKTM ($T_g = 144$ °C) and tert-butyl PEEK ($T_g = 176$ °C). In fact, TMBP is the bisphenol of choice when high T_g and large permeabilities are required. The same effect can be seen with the polysulfones (Table I.2).

Table I.1. T_g and Gas Transport Properties for Substituted PEEK⁴⁹

-Ar- T_g (°C)	P(O ₂) Barrers	α (O ₂ /N ₂)	P(CO ₂) Barrers	α (CO ₂ /CH ₄)
 $T_g = 144$; T_m 335	0.259	6.5	0.963	31
 $T_g = 176$	1.39	6.4	4.65	21
 $T_g = 240$	4.76	4.9	19.6	19

Polysulfones generally exhibit better solubilities, higher T_g s and permeabilities than their poly(aryl ether ketone) counterparts for reasons discussed already. This has led to their more frequent study as gas membranes and thus more ready availability of data in the literature.⁴³⁻⁴⁵ Table I.2 lists gas permeability and T_g data for a series of polysulfones differing only in their bisphenol unit.⁵⁰ Acronyms have been included for easy reference in the text.

As noted for the polyketone series, the polymer made with TMBP displays the largest permeabilities and T_g within the series of polysulfones ($T_g = 288\text{ }^\circ\text{C}$). The biphenol (BP) polymer is provided for direct comparison to the TMBP unit. It has a lower glass transition temperature ($T_g = 230\text{ }^\circ\text{C}$) and reduced permeabilities, about 1/5 to 1/6 the permeabilities of the tetramethyl substituted polysulfone. The decrease in selectivities for the TMBP-based polysulfone appear less pronounced than in the polyketone case. In fact, a slight increase in CO_2/CH_4 selectivity is observed.^{50a}

The BPA-containing polysulfone (UDELTM) ($T_g = 185\text{ }^\circ\text{C}$) compares well in gas transport properties to the BP-based one but has a lower T_g of $230\text{ }^\circ\text{C}$ due the presence of the flexible isopropylidene group in its mainchain. Since UDELTM is used commercially as a gas membrane, it is often used as a benchmark for comparison to other polymers in gas transport studies.^{50b}

Substituting hydrogen atoms of the isopropylidene unit in BPA with larger fluorine atoms (i.e. 6F-BPA) increases T_g slightly ($T_g = 192\text{ }^\circ\text{C}$) and increases permeability 2 and 3 fold for CO_2 and O_2 permeabilities. This is because 6F-BPA sterically hinders both bond

rotation and intersegmental packing. The packing of 6F-BPA may also further inhibited by the repulsive forces between fluorine atoms which are areas of high electron density.^{50c}

The introduction of a kink or 'bend' into the polysulfone mainchain via meta substitution within the BPA unit (i.e. MBPA) significantly reduces its glass transition temperature ($T_g = 156\text{ }^{\circ}\text{C}$) and gas permeabilities with marginal improvements to selectivity. The authors reasoned that gas permeabilities are reduced because meta substitution imparts mobility constraints which lead to better intermolecular packing and smaller free volumes.^{50d}

Three dihydroxy naphthalenes (1,5-, 2,6- and 2,7-) were used to study the isomeric effects of naphthylene insertion into polysulfones. Like the meta substitution, the permeabilities for O_2 and CO_2 decreased (in the order 1,5- > 2,6- > 2,7-) when compared to the BPA-based polysulfone and their corresponding selectivities increased. Their selectivities increased so much that the separation factors for CO_2/CH_4 are reported to be the highest of any polysulfone studied to date. And, unlike meta substitution, naphthyl insertions result in polysulfones with higher T_g ($240\text{ }^{\circ}\text{C}$, $227\text{ }^{\circ}\text{C}$, $215\text{ }^{\circ}\text{C}$ respectively) than the BPA-type polysulfones.^{50e}

Table I.2. T_g and Gas Transport Properties of PAES⁵⁰

-Ar- T_g (°C)	P(O ₂) Barrers	α (O ₂ /N ₂)	P(CO ₂) Barrers	α (CO ₂ /CH ₄)
 BP: 230 ^{50a}	1.3	5.5	5.6	22
 TMBP: 288 ^{50a}	5.8	4.8	31.8	25
 BPA: 185 ^{50b}	1.4	5.6	5.6	22
 6F-BPA: 192 ^{50c}	3.4	5.4	12	22
 MBPA: 156 ^{50d}	0.39	5.9	1.5	29
 1,5-NAP: 240 ^{50e}	0.4	7.4	1.6	44
 2,6-NAP: 227 ^{50e}	0.38	7.5	1.5	41
 2,7-NAP: 215 ^{50e}	0.50	6.8	1.8	36

To compliment some of the T_g data presented already for the PAES, Table I.3 lists T_g for equivalent PEAK where permeabilities were not available in the literature and for additional bisphenols previously not discussed. Bisphenols containing bulky cardo groups, such a phenolphthalein (PP) and 9,9-bis(4-hydroxyphenyl)fluorene (HFP), tend to break the stacking ability of the polymer making them more soluble and processable.^{26a} The

bulky nature of these bisphenols also leads to significant increases in T_g and improved solubilities for both PAEK and PAES.

Table I.3. Influence of Bisphenols on T_g s of PAEK and PAES^{2,50a}

PAEK (Z = CO) T_g (°C)	-Ar-	PAES (Z = SO ₂) T_g (°C)
144; $T_g = 335^2$	HQ	217, $T_m = 310^2$
214 ²	PP	272 ²
252 ²	HFP	280 ²
155 ²	BPA	185 ²
170 ²	BP	220 ²
240 ²	TMBP	288 ^{50a}
175 ²	6F-BPA	192 ^{50c}

1.3.2. Structural Modifications of Dihalide Monomers

Although traditional modifications of poly(aryl ether ketone)s have focused on variations to the bisphenols, recently some researchers have designed unique dihalo activated monomers for polyetherifications.^{51,52}

Mercer⁵¹ and co-workers incorporated two 1,4-naphthylene moieties into a symmetrical di(fluoroketone) monomer containing a 6F-BPA unit (Figure I.15) and polymerized it with various bisphenols. Glass transition temperatures are shown for three bisphenols in Figure I.15. It was found that these polymers had improved solubilities and T_g s when compared to other PAEK. Mercer attributed these favorable properties due to the presence of the flexible 6F-BPA unit and the presence of the bulky 1,4-naphthylene unit which inhibits crystallization and allows the penetration of solvent molecules.

Figure I.15. Symmetrical 1,4-naphthylene containing difluoro monomer⁵¹

Wang and co-workers⁵² developed two new dihalo keto monomers (Figure I.16) which served to incorporate 1,4-naphthylene into two new series of symmetric poly(aryl ether ketone)s when polymerized with various bisphenols. When compared to their 1,4-phenylene equivalents, increases in T_g varied from $\sim 20^\circ\text{C}$ to as high as 89°C (Table I.4).

Figure I.16. Symmetrical 1,4-naphthylene containing monomers⁵²Table I.4. T_g (°C) of Symmetrical 1,4-Naphthylene Containing Polymers⁵²

T_g (°C) $R = -\text{C}(=\text{O})-\text{C}_6\text{H}_4-\text{C}(=\text{O})-$	-Ar-	T_g (°C) $R = -\text{C}(=\text{O})-$
217		232
230		235
204		212
265		273

I.4. Rationale and Objectives

A commonly held philosophy amongst innovative chemists is that novel structured polymers will lead to polymers containing unique properties. In fact, where would humankind be today if scientists had not sought to create new materials, such as nylon, polystyrene, polycarbonate and polyester, which permeate our everyday existence? Subscribing to the above philosophy, the overall goal of this thesis is to create changes on the molecular level of a polymer and study the effects on the macroscopic properties of the polymer.

In order to make changes on a polymer's microstructure, structural features must be built into the monomer. As mentioned already, most changes made to date have focused on the bisphenol unit of poly(aryl ether)s made by aromatic nucleophilic substitution polymerization. This thesis proposes to incorporate the following structural features into several poly(aryl ether)s.

Figure I.17. Design of structural features

In doing so, several novel activated dihalide monomers are designed and polymerized with various bisphenols and polymer properties are studied. Where possible, comparisons are made with equivalent commercial phenyl-based polymers. The designs of the dihalide monomers are rationalized according to the following reasons.

L4.1. 1,4-Naphthylene-Based Polymers

The naphthalene ring offers increased thermal stability over its phenyl equivalent due to its increased aromaticity. Therefore, it is expected that the naphthalene-containing polymers are thermally robust. There also exists some precedent in the literature that inserting 1,4-naphthylene in a polymer backbone will increase its glass transition temperature.^{50e,51} Therefore it is hypothesized that the glass transition temperatures of the polymers containing the 1,4-naphthylene unit will be higher than most 1,4-phenylene equivalent polymers.

To date, most gas transport studies have investigated the effects of aliphatic pendant groups attached to a polymer's main chain. In the cases where naphthylene is incorporated, isomers other than 1,4-substitution were used.^{50e} The insertion of 1,4-naphthylene^{51,52} serves as the addition of a pendant group, in this case, the benzo unit, perpendicular to the polymer mainchain. This is predicted to increase the polymer's free volume and therefore its permeability.

In the cases where 1,4-naphthylene insertion has been reported,^{51,52} the monomers were symmetrical in nature. But when the phenyl ring of the commercially available 4,4'-difluorophenyl ketone is replaced by a 1,4-naphthylene unit, an unsymmetric monomer results (Figure I.18). To date, only symmetric monomers have been studied thus it would be interesting to investigate what effect unsymmetry will have on the properties of the polymer.

Figure I.18. Symmetric and unsymmetric 1,4-naphthylene-based monomers

The 1,4-naphthylene group also seemed a worthy candidate considering the many resonance forms available to the Meisenheimer complex (Figure I.19). As discussed previously, the more stabilized the Meisenheimer complex, the more reactive it is to polymerization. The phenylene-containing Meisenheimer complex results in two principal resonance structures whereas the 1,4-naphthylene-containing monomers have more possible Meisenheimer resonance structures favoring polymerization.

Figure I.19. Possible resonance structures of 1,4-naphthylene-containing Meisenheimer complexes

I.4.2. 1,1'-Binaphthalene-Based Polymers

A logical extension to the work involving 1,4-naphthylene is the incorporation of a binaphthalene unit into the polymer. Similar thermal stability and increases in T_g are expected as with 1,4-naphthylene insertion.

Subscribing to the philosophy that unique polymer properties can arise from careful design at the molecular level, several characteristics inherent to the ortho substituted 1,1'-binaphthylene unit are expected to be translated into the polymer's properties. 1,1'-Binaphthyl compounds contain axial chirality and display modest optical activities.⁵³ A polymer which incorporated this unit would also be expected to have similar

characteristics. The incorporation of the binaphthyl unit into an appropriately activated dihalide monomer seemed feasible. The particulars of this design will be disclosed in chapter four.

Helicenes are typically fluorescent and exhibit higher optical activities than 1,1'-binaphthyls.⁵⁴ Helicene-containing polymers would be expected to display similar characteristics and be potentially useful as chiroptical materials. Yet helicenes are arduous to make, contain no electron withdrawing groups for monomer activation and are difficult to functionalize for polymerization. To circumvent the difficulty in synthesizing an activated helicene monomer directly, a post-polymer transformation can be visualized for the precursor binaphthyl-containing poly(aryl ether) based on some known chemistry (Figure I.20).⁵⁵ If successful, this will demonstrate a unique axial-to-helical chirality transformation in poly(aryl ether)s.

Figure I.20. Design of 1,1'-binaphthalene and helicene-containing PAE

In summary, the objectives of this thesis work are:

1. To synthesize new ketone and sulfone activated dihaloaryl monomers containing the 1,4-naphthylene and 1,1'-binaphthalene moieties.

2. To polymerize the uniquely structured dihaloaryl monomers with various bisphenols to form new series of PAEK and PAES.
3. To study the effects which the designed structural features have on their macroscopic properties.
4. To investigate a new route to introduce [5]helicenes into the repeat unit of poly(aryl ether)s from a binaphthalene-based poly(aryl ether ketone).

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II.1. Introduction

Aromatic polysulfones are among the most heat resistant of current commercial thermoplastics. Three polysulfones of great commercial utility are Union Carbide's Udel™ and Radel R™ and ICI's Victrex™ (Figure II.1).^{1,2} They are available in a variety of forms such as molded parts, films, fibers and coatings for applications as car engine parts, electrical components, sterilizable medical equipment and household molded products.^{3,4} Polysulfones, such as Udel™, have also been used as membranes for gas separation with varying degrees of success.^{5,6} Yet, much effort is still needed in order to better understand the relationships between polysulfone structures and resulting thermal, mechanical and gas transport properties.^{5,6}

Figure II.1. Structures of commercial polysulfones

The insertion of the 1,4-naphthylene group was proposed as a means to disrupt chain packing, improve processability, enhance gas transport properties and increase thermal stability. Its incorporation was accomplished through the design and synthesis of a

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unique unsymmetric dihaloarylsulfone, 1-chloro-4-(4-fluorobenzenesulfonyl)naphthalene **II-1**, as outlined in Scheme II.1.

Chapter one showed that a monomer containing the 1,4-naphthylene group provided greater stabilization to the Meisenheimer intermediate through its many resonance structures, therefore will be more reactive towards nucleophilic substitution.

In addition, Hückel molecular orbital (HMO) calculations were performed to evaluate the reactivity of the target monomer.⁷ Hückel molecular orbital (HMO) calculations can give the partial positive charge density at the carbon bearing the halide. The greater the net charge, the more reactive it is towards nucleophilic displacement polycondensation. These calculations, although not always accurate, help to predict reactivities of unknown monomers.

The known monomers, 4-fluorophenylsulfone and 4-chlorophenylsulfone, have net charges of 0.041 and 0.017, respectively, at the carbon attached to the halogen (Figure II.2). HMO calculations thus confirm the greater reactivity of fluorine over chlorine for the sulfone series of symmetrical monomers. And yet, the less expensive chlorine derivative is used in the commercial production of polysulfones because of its suitable reactivity.¹ So a minimum requirement of 0.017 for the net charge density of the halogen bearing carbon in dihalo activated sulfone monomers seems in order.

Figure II.2. Charge densities of known dihalide monomers

HMO calculations showed net charge densities of 0.032 and 0.042 on the carbons ipso to the halogens in monomer **II-1** indicating its suitable reactivity (Figure II.3). In fact, the naphthyl ring seemed to significantly increase the reactivity of the carbon attached to the chlorine atom relative to the phenyl ring. This concept will be explored further with the poly(aryl ether ketone) series in chapter three.

Figure II.3. Charge densities of proposed sulfone monomer **II-1**

The sulfone monomer was then polymerized with various bisphenols and one heterocyclic monomer to obtain a new series of unsymmetric PAES containing the 1,4-naphthylene moiety (Scheme II.2).

The poly(aryl ether sulfone)s made with BPA and BP are structural analogues of Udel and Radel R, whereas the BPS-based unsymmetric polysulfone contains the naphthylene moiety in every second repeating unit of Victrex polysulfone. Rose et al. had already replaced one para-phenylene groups in each repeating unit of Victrex with the 1,4-naphthylene moiety⁸ and found that the glass transition temperature increased but that the material still displayed some crystallinity ($T_g = 238\text{ }^{\circ}\text{C}$, $T_m = 367\text{ }^{\circ}\text{C}$).

II.2. Monomer Synthesis and Characterization

II.2.1. Synthesis

The unsymmetric dihalo sulfone monomer **II-1** can be synthesized by the Friedel-Crafts reaction of 1-chloronaphthalene-4-sulfonyl chloride with fluorobenzene or by the reaction of 4-fluorobenzenesulfonyl chloride with 1-chloronaphthalene (Figure II.4).

Figure II.4. Retrosynthetic routes to sulfone monomer **II-1**

The one step sulfonylation reaction between 1-chloronaphthalene and 4-fluorobenzenesulfonyl chloride was attempted first. Both AlCl_3 and FeCl_3 were used as catalysts at 0 °C and room temperature with dichloroethane as the solvent. It was possible to make the target monomer, but the presence of two isomers and unreacted 1-chloronaphthalene, as detected by TLC and HPLC, in the reaction mixture made it difficult to purify resulting in low yields (<15%). Increasing the temperature to 80 °C only increased the presence of the isomers. Thus a second route was pursued.

Sulfonylation of fluorobenzene with 1-chloronaphthalene-4-sulfonyl chloride was found to produce **II-1** in high purity.⁹ The intermediate, 1-chloronaphthalene-4-sulfonyl chloride, was obtained from the corresponding aminonaphthalene sulfonic acid by diazotization and the Sandmeyer reaction followed by treatment with phosphorus oxychloride (Scheme II.1).¹⁰ Recrystallization twice from toluene afforded colorless crystals with a m.p. of 196-199 °C.

Scheme II.1. Synthesis of sulfone monomer II-1

II.2.2. Characterization

MS indicated a molecular ion peak of 320 with fragmentation peaks at 221, 161 and 126. IR showed peaks at 1318 and 1140 cm^{-1} which were due to S=O asymmetric and symmetric stretching.

Assignment of the ^1H NMR spectrum of monomer II-1 was possible in conjunction with the COSY experiment and is shown in Figure II.5. Heteronuclear ^1H - ^{19}F coupling is observed in the ^1H NMR spectrum due to the presence of the fluorine atom which has a nuclear spin state of 1/2. The proton labeled Ha appears as a triplet at 7.14 ppm with equal coupling constants of 8.6 Hz with neighbouring proton Hb and the fluorine atom. The proton labeled Hb appeared as a doublet of doublets at 7.96 ppm, being split by adjacent Ha proton ($^3J_{\text{H-H}} = 8.6$ Hz) and by the distal fluorine atom ($^4J_{\text{H-F}} = 5$ Hz).

Assignments of key peaks in the ^{13}C NMR spectrum, using HETCOR experiments, are given in Table II.2. The carbon attached to the fluorine atom (C-1) appeared as a doublet centered at 116.39 ppm with a $^1J_{\text{C-F}}$ value of 255 Hz. Similarly, the carbon ortho to the fluorine atom (C-2) showed as a doublet centered at 116.38 ppm with a $^2J_{\text{C-F}}$ value of 23 Hz, and the fluorine's meta carbon (C-3) showed a doublet at 130.26 ppm with a $^3J_{\text{C-F}}$ value of 9 Hz. The carbon 'para' to the fluorine atom (C-4) appears as a finely split doublet at 137.64 ppm with a $^4J_{\text{C-F}}$ of 4 Hz. The remaining peaks are difficult to identify

Figure II.5. The 400 MHz ¹H NMR spectrum (7.0 to 8.8 ppm) of sulfone monomer **II-1**

specifically but add up to the appropriate number of quaternary and methine carbons.

The ^1H and ^{13}C NMR chemical shifts were estimated by adding the substituent effects¹¹ based on the structures given in Figure II.6. Estimated chemical shifts are compared to experimental values in Table II.1 and Table II.2. The 1-chloronaphthyl ring was approximated by substitution with the 1-chlorophenyl ring, thus it was not possible to calculate chemical shifts for the bottom portion of the naphthalene ring.

Figure II.6. 4-Fluoro- and 4-chlorophenyl moieties used in ^1H and ^{13}C NMR estimations

A strong correlation exists between the estimated and experimental NMR chemical shifts for protons Ha and Hb and carbons C-1, C-2, C-3 and C-4 of the fluorobenzoyl ring. Conversely, it appears that estimations based on the substitution of the naphthyl ring by a phenyl unit strongly compromises the chemical shift values of protons Ha' and Hb' of the chloronaphthyl moiety. And yet, estimations of the naphthyl portion in the ^{13}C NMR spectrum were very close to the experimental assignment (represented by C2' and C3'). In final, although not always correct in magnitude for the naphthyl portion, the estimated values seem to be correct on a relative scale based on assignments from HETCOR and COSY experiments.

Table II.1. Comparison of Estimated and Experimental ^1H NMR Chemical Shifts.

II-1	HA	HB	HB'	HA'
exptl	7.14	7.96	8.43	7.72
δ, J	^3J 8.6 Hz ^3J 8.6 Hz	^3J 8.6 Hz ^4J 5.0 Hz	^3J 8.0 Hz	^3J 8.0 Hz
calc, δ^{11}	7.23	7.86	7.86	7.55

Table II.2. Comparison of Estimated and Experimental ^{13}C NMR Chemical Shifts.

II-1	C-1	C-2	C-3	C-4	C-3'	C-2'
exptl	165.39	116.58	130.26	137.64	129.77	124.99
$\delta, \text{J}_{\text{C-F}}$	^1J =255Hz	^2J =23 Hz	^3J =9 Hz	^4J =4 Hz		
calc, $\delta^{[3]}$	168.1	116.5	129.0	137.1	128.9	129.6

Recently, both ^{19}F and ^{13}C NMR spectroscopy have been used to probe the reactivity of potentially activated fluoride monomers due to their ability to measure the electronic density at the site of nucleophilic reaction.¹² Figure II.7 shows relevant ^{13}C and ^{19}F NMR chemical shifts of known monomers.¹³ Again, the expected superior reactivity of the fluorine monomer is corroborated by its more deshielded value (by ~25 ppm) than the chloro-attached carbon.

Figure II.7. ^{13}C and ^{19}F NMR chemical shift values¹³

The carbon ipso to the fluorine atom has a chemical shift of 165.4 ppm which is well in the range of 4-fluorophenylsulfone's value of 165.3 ppm (Table II.2). It is difficult to identify the carbon attached to the chlorine atom from the other quaternary carbons in monomer **II-1** and so the reactivity of this side of the monomer is still uncertain.

Further evidence confirming the reactivity of the fluoride side of the monomer comes from ^{19}F NMR data. The literature reports a peak at -104.08 ppm for the fluorine atom in 4-fluorophenylsulfone.¹³ The ^{19}F NMR spectrum showed a singlet at -104.38 ppm relative to CCl_3F for the unsymmetric monomer **II-1** indicating not only its purity, but its sufficient activity.

II.3. Polymer Synthesis and Characterization

II.3.1. Synthesis

Polymers **II-3(a-h)** were obtained by the polycondensation reaction of monomer **II-1** with eight different bisphenols **II-2(a-h)**, i.e. 4,4'-(isopropylidene)diphenol (BPA), 4,4'-(hexafluoroisopropylidene)diphenol (6F-BPA), 4,4'-biphenol (BP), 2,2',6,6'-tetramethyl-4,4'-biphenol (TMBP), bis(4-hydroxyphenyl)sulfone (BPS), 1,4-hydroquinone (HQ), 9,9-bis(4-hydroxyphenyl)fluorene (HFP) and phenolphthalein (PP) (Scheme II-2).^{9,14}

Scheme II.2. Polymerization of the sulfone monomer to give **II-3(a-i)**^{9,14}

Polymerizations were all done in TMSO₂ with chlorobenzene as an azeotroping agent at 200 °C using stoichiometric amounts of the dihalide and bisphenol monomer in the presence of potassium carbonate (1.8 molar equivalent). Typically, the reaction was heated from room temperature to 140-150 °C within 0.5 to 1 h and the water formed during the reaction was removed as an azeotropic mixture with chlorobenzene. The polymerization temperature was then increased to 200 °C and the reaction proceeded for 3 h before GPC monitoring showed no further increase in molecular weight and the reaction was stopped. The resulting polymers were coagulated in an excess of methanol with a few drops of concentrated HCl, followed by reverse precipitation to remove any remaining oligomers.

In addition, monomer **II-1** was polymerized with 1,2-dihydro-4-(4-hydroxyphenyl)(2H)phthalazin-1-one (**II-2i**). Unlike the bisphenols, the heterocyclic monomer polymerizes activated aryl halides via a N-C coupling reaction using the azanitrogen anion formed *in-situ* in the presence of base (Scheme II.3).¹⁵ Poly(aryl ether)s made from this monomer are characterized with high T_g due to its rigidity.

Scheme II.3. Synthesis of phthalazinone-based PAE¹⁵

II.3.2. Molecular Weights

Gel permeation chromatography (GPC) was used to measure the molecular weights of polymers **II-3(a-i)** relative to polystyrene standards (Table II.3).

Table II.3. Molecular Weights and Inherent Viscosities of PAES II-3(a-i)

Polysulfone	Bisphenol	$M_w^a \times 10^{-4}$	$M_n^a \times 10^{-4}$	M_w/M_n	η_{inh} (dL/g)
II-3a	BPA	15.1	9.67	1.56	0.75 ^b
II-3b	6F-BPA	8.97	5.50	1.63	0.46 ^b
II-3c	BP	8.33	4.16	2.00	0.70 ^b
II-3d	TMBP	15.6	7.72	2.02	1.09 ^b
II-3e ^d	BPS	0.80	0.29	2.72	0.40 ^c
II-3f	HQ	7.29	3.36	2.17	n/o ^c
II-3g	HBP	15.33	8.43	1.81	0.70 ^b
II-3h	PP	25.4	14.0	1.81	0.71 ^b
II-3i	PZ	8.01	4.77	1.68	0.37 ^b

^a Taken by GPC relative to polystyrene standards.

^b Inherent viscosity, 0.5 % chloroform solution at 25.0 °C.

^c Inherent viscosity, 0.5% TCE solution at 25.0 °C.

^d polymerization attempted three times, not reverse precipitated, contained oligomers.

^e not obtained.

With the exception of II-3e, results showed all the polymers in the series II-3 (Scheme II.2) were of high molecular weight. Molecular weights (M_w) ranged from a minimum of 7.29×10^4 for the 1,4-hydroquinone-based II-3f to a maximum of 25.4×10^4 for the phenolphthalein-derived II-3h. Polymerization of bis(4-hydroxyphenyl)sulfone (BPS) with monomer II-1, to form PAES II-3e, was tried three times but was not successful in attaining a high molecular weight ($M_w = 0.80 \times 10^4$) and was not reverse precipitated. This poor polymerization agrees with the fact that BPS is the least reactive among common commercially available bisphenols towards polymerization with 4,4'-

dichlorodiphenylsulfone presumably because of the strong electron withdrawing power of the sulfone group.¹⁵ Polymer **II-3e** has the largest M_w/M_n ratio because it still contains lower molecular weight fractions. The inherent viscosities supported the GPC results with values ranging from 0.40 to 1.09 dL/g (Table II.3). Indeed, with the exception of deactivated BPS, monomer **II-1** was found to be extremely polymerizable with most commercially available bisphenols.

II.3.3. Characterization

All polymers were obtained as off-white, fibrous solids. Most were soluble at room temperature in chloroform, 1,1',2,2'-tetrachloroethane (TCE), CH_2Cl_2 , N-methylpyrrolidinone (NMP), tetrahydrofuran (THF), N,N-dimethylformamide (DMF) and (DMAc) with a few exceptions (Table II.4). One being the TMBP-based polymer, **II-3d**, which was only partially soluble in DMF. The HQ-based and BPS-based polymers, **II-3f** and **II-3e**, were only partially soluble in THF. The BP-based polymers, **II-3c**, was the least soluble having difficulty dissolving in THF and DMF. It is known that the biphenyl moiety promotes chain packing, as the symmetric BP-based ketone polymer is semi-crystalline with a T_m of 416 °C. Due to the tetrahedral sulfone unit, polymer **II-3c** showed higher solubility than the unsymmetric ketone analogue **III-3c**.

The IR spectrum of each sulfone polymer showed strong peaks at $\sim 1240\text{ cm}^{-1}$ and $\sim 1146\text{ cm}^{-1}$ which corresponds to the expected sulfone asymmetric and symmetric stretching.

The ^1H and ^{13}C NMR data for polymers **II-3(a-h)** are provided in the experimental section. The NMR spectra of the phthalazinone-based polymer **II-3i** was

performed but was too unresolved to decipher, even with HETCOR and COSY experiments, thus its data are not included.

Table II.4. Solubilities of PAES **II-3(a-i)**^a

Polymer	CHCl ₃	TCE	CH ₂ Cl ₂	NMP	THF	DMF	DMAc
II-3a	+	+	+	+	+	+	+
II-3b	+	+	+	+	+	+	+
II-3c	+	+	+	+	+/-	+/-	+
II-3d	+	+	+	+	+	+/-	+
II-3e	+	+	+	+	+/-	+	+
II-3f	+	+	+	+	+/-	+	+
II-3g	+	+	+	+	+	+	+
II-3h	+	+	+	+	+	+	+
II-3i	+	+	+	+	+	+	+

^a Solubilities taken of 10-20 mg sample of polymer in 1-2 mLs of solvent.

‘+’ fully soluble at room temperature, ‘+/-’ partially soluble at room temperature

The aromatic region of the ¹H NMR spectrum of the BPA-based polymer **II-3a** is assigned based on COSY experiments (Figure II.8). The NMR spectra of polymers **II-3(a-h)** are simplified relative to the monomer spectrum in the absence of ¹H-¹⁹F coupling. Yet, there exists a unique situation where three different diads are possible, due to the polymerization of the unsymmetric dihalo monomer with a symmetric bisphenol in a) head to head, b) head to tail and c) tail to tail fashion. Figure II.9 illustrates the three different local magnetic environments the methyl groups of BPA find themselves in polymer **II-3a**. Evidence of these three diads can be seen clearly in the aliphatic region of the ¹H NMR

spectrum (Figure II.9). The BPA polymer showed three methyl singlets peaks in the 1.7 ppm region in an approximate ratio of 1:2:1. Protons in the aromatic region, such as H_i and H_j, also seem to experience different magnetic environments and do not appear as simple doublets (Figure II.8). ¹³C NMR of **II-3a** also showed fine splitting of the aliphatic quaternary carbon (42.77, 42.75 and 42.73 ppm).

The structures of the three diads of the TMBP-based polymer **II-3d** are shown in Figure II.10. The aliphatic region displayed four singlets centered at ~2.15 ppm in the ¹H NMR spectra (Figure II.10) and four aliphatic carbon peaks (16.47, 16.45, 16.32 and 16.30 ppm) in the ¹³C NMR spectrum. Unlike the BPA case, the methyl groups of TMBP are located in four different magnetic environments in the head-to-head, tail-to-tail and head-to-tail diads (Figure II.10). In the head-to-head and tail-to-tail formations, all four methyl groups are either closer to a naphthylene ring or a phenylene ring and therefore are in two different magnetic environments corresponding to two of the four singlets. In the head-to-tail diad, two of the methyl groups are closer to a naphthylene ring, whereas the other two are closer to a phenylene ring, thereby giving rise to the presence of the remaining two proton peaks. The intensities of the outer two peaks appear the same, likewise with the smaller inner two peaks. The unsymmetric nature of the other polymers is also seen by the additional peaks in their ¹³C NMR spectrum.

Figure II.8. The 400 MHz ^1H NMR spectrum (6.8 - 8.7 ppm) of PAES **II-3a**

Figure II.9. Three diads of (a) BPA-based PAES II-3a and 400 MHz ^1H NMR spectrum (1.6 to 1.8 ppm)

Figure II.10. Three diads of TMBP-based PAES II-3d and 400 MHz ^1H NMR spectrum (2.0 to 2.3 ppm)

UV/VIS spectra were taken of polymers **II-3(a-i)** and monomer **II-1** in chloroform. All the polymers showed a peak between 302-311 nm. All but **II-3i** showed a peak at 241 nm and all but **II-3a** and **II-3d** showed a third peak at 260-265 nm. The sulfone monomer **II-1** had two major peaks at 241.5 nm and 302.8 nm. The broad peak at 302-311 nm is due to π - π^* transitions of the naphthyl ring. The sharp peak at 241 nm is due to π - π^* transitions of the phenyl ring. The third peak at 260- 265 nm seen in all, but the BPA and 6F-BPA polymers, is due to π - π^* transitions of the specific bisphenol used in each case.

II.4. Polymer Properties

II.4.1. Thermal and Mechanical Properties

Glass transition temperatures (T_g) of polysulfones **II-3(a-i)** taken using differential scanning calorimetry (DSC) were in the range of 218 °C to 317 °C. A comparison of the T_g s of the unsymmetric polysulfone series **II-3(a-i)** versus its symmetric equivalent is made in Table II.5. In each case, 1,4-naphthylene insertion causes an increase in T_g compared to its symmetric counterpart. Increases in T_g were significant (>22 °C) for **II-3 (a, c, d, f, h and i)** and moderate ($8^\circ\text{C} < \Delta T_g < 14^\circ\text{C}$) for **II-3 (b,e and g)**. Most notable, is the glass transition temperature over 300 °C for the phthalazinone-based polysulfone **II-3i** ($T_g = 317$ °C). The high glass transition temperature is possible due to the increased rigidity of the heterocyclic monomer and has been noted for other poly(aryl ether)s containing this monomer.¹⁵

Most polysulfones are amorphous with notable exceptions being (a) Victrex and (b) an analogue of Victrex made by Rose and co-workers which contains 1,4-naphthylene in each repeat unit (Figure II.11).⁸ Yet DSC results showed that all nine polymers, **II-3(a-i)**, appeared amorphous. Therefore the amorphous nature of **II-3e** can be best explained by a combination of: (a) the effective disruption to chain packing imposed by 1,4-naphthylene insertion into every *second* repeat unit and (b) the presence of several different microstructures mentioned in section II.3.3.

Table II.5. T_d of 1,4-Naphthylene-based PAES **II-3(a-i)** and Comparison of T_g with 1,4-Phenylene-based PAES

Polysulfone			ΔT_g (°C) ^c	T_d (°C) ^d
II-3a	218	"Udel" 185 ¹	33	470
II-3b	219	192 ^{16a}	14	471
II-3c	250	"Radel R" 230 ^{16b}	20	470
II-3d	309	288 ^{16b}	21	390
II-3e	234	"Victrex" 220 ¹	14	466
II-3f	234	210 ¹	24	468
II-3g	288	280 ¹	8	491
II-3h	280	244 ^{16c}	36	446
II-3i	317	295 ^{15a}	22	463

^a Glass transition temperature (°C) of unsymmetric naphthylene-containing polysulfone

^b Glass transition temperature (°C) of symmetric phenylene-containing polysulfone

^c The increase in T_g of unsymmetric polysulfone over symmetric polysulfone

^d The decomposition temperature at 5% weight loss.

Figure II.11. Comparison of T_g for Victrex™ and 1,4-naphthylene-containing PAES

Decomposition Temperature

The decomposition temperature as assessed by the onset temperature (T_d) of 5% weight loss by TG occurred in the range of 390–491°C in nitrogen. The polymer which displayed the lowest T_d by more than 50 °C is **II-3d** ($T_d = 390^\circ\text{C}$). The presence of TMBP is believed to impart thermal instability due to the presence of four methyl groups in the repeat structure.

Young's Moduli

Thin rectangular strips of polymer films cast from chloroform solution were used to measure Young's modulus in the tensile stress-strain mode. The moduli varied from 0.54–1.68 GPa for the selected polysulfones (Table II.6). The Young's modulus of Udel was found to be 2.9 GPa. When compared to **II-2a**, its unsymmetric equivalent, it appeared that 1,4-naphthylene insertion decreased the tensile strength for this particular polysulfone.

Table II.6. Young's Moduli of Various Unsymmetric PAES

Polysulfone	II-3a	II-3c	II-3d	II-3g	II-3h
Bisphenol	BPA	BP	TMBP	HBP	PP
E' (GPa)	0.39	0.41	0.41	1.68	0.54

II.4.2. Gas Transport Properties

A gas molecule is believed to dissolve and diffuse through a polymer membrane thereby involving a solution-diffusion mechanism.^{17,18} Permeability (P) is therefore expressed as the product of diffusivity (D) and solubility (S) i.e. $P = D \times S$. Selectivity (α) is a measure of a polymer's ability to discriminate between different gas molecules. It is expressed as the ratio of a polymer membrane's permeability towards two separate gases i.e. $\alpha_{ab} = P_a/P_b$ where α_{ab} is the separation factor of a membrane towards gas 'a' and 'b'.

Chapter one stipulated that for a gas membrane to be successful, it must combine both high permeability and high selectivity. And yet, structural features which favor one usually come at the cost of lowering the other and so a compromise must be made. To date, most gas transport studies have investigated the effects of aliphatic pendant groups attached to the main chain of a polysulfone. This section investigates the effect 1,4-naphthylene insertion has on the gas transport properties of the BPA- and TMBP-based polysulfones (II-3a and II-3d). The BPA-containing polysulfone II-3a is the 1,4-naphthylene analogue of UDELTM and II-3d is the 1,4-naphthylene analogue of the TMBP-based polysulfone shown in Figure II.12.

Figure II.12. Structural 1,4-naphthylene analogues of UDEL and TMBP-based PAES

Tough dense films were cast from chloroform solution of **II-3a** and **II-3d** in order to study their gas transport properties. Gas transport properties are compared with compared with their 1,4-phenylene equivalent in Table II.7.

Results show that the oxygen/nitrogen permselectivity of **II-3a** ($\alpha(\text{O}_2/\text{N}_2) = 8.0$) was marginally improved over Udel's ($\alpha(\text{O}_2/\text{N}_2) = 5.0$) at the cost of lowering the permeability of each gas (Table II.7). The increase in permselectivity for carbon monoxide/methane over UDEL ($\alpha(\text{CO}_2/\text{CH}_4) = 22$) was even larger ($\alpha(\text{CO}_2/\text{CH}_4) = 59$). This permselectivity is higher than the 1,5-, 2,6-, and 2,7-naphthylene-based PAES reported in chapter one (Table I.2). Again the increase came at the cost of lower permeability, i.e. $P(\text{CO}_2)$ of 4.7 Barrer for **II-3a** as opposed to $P(\text{CO}_2)$ of 5.6 Barrer for UDEL. It should also be noted that the downstream pressure leveled off after about 24 h during measurement of methane gas. It is possible that the large methane molecules saturated the naphthylene-containing polysulfone membrane, impeding passage of further gas molecules. Thus, the apparent increase in permselectivity for carbon monoxide/methane is questionable.

The gas permeabilities of the TMBP series (**II-3d** and phenylene equivalent) are much larger than those of the polymers derived from BPA as expected.^{16b} And as noted before,^{16b} the increase in permeability came as a tradeoff of reducing the selectivity coefficients relative to the BPA polysulfones. Yet when compared to the phenylene equivalent, the 1,4-naphthylene-based polysulfone **II-3d** seems to marginally improve permselectivities making this polymer more suitable for gas membrane use.

Table II.7. Gas Transport Properties of 1,4-Phenylene and 1,4-Naphthylene-Based PAES

	^a P _{O₂} Barrer	P _{N₂} Barrer	^c α(O ₂ /N ₂)	P _{CO₂} Barrer	P _{CH₄} Barrer	α (CO ₂ /CH ₄)
II-2a	1.21	0.15	8.0	4.7	0.08 ^c	59
II-2d	5.90	1.09	5.4	27.0	0.97	28
Udel ²⁰	1.4	0.3	5.6	5.6	0.3	22
TMBP ^{16b}	5.8	1.21	4.8	31.8	1.27	25

^a P is the gas permeability with the specified gas, taken at 150 psi.

^b α is the gas permselectivity towards the specified gas pair.

^c Steady state condition appeared to level off after 24h. Slope was taken between 8h and 16h where the 3θ - 6θ region was estimated.

II.5. Conclusions

The design and synthesis of a novel unsymmetric dihaloarylsulfone monomer **II-1** was successfully performed through the Friedel-Crafts reaction of fluorobenzene and 1-chloronaphthalene-4-sulfonyl chloride in 25% overall yield. Polymerization of **II-1** with various bisphenols created a new series of poly(aryl ether sulfone)s **II-3(a-h)** containing the 1,4-naphthylene unit in the mainchain.

In all cases, incorporation of the 1,4-naphthylene group stiffens the polymer backbone, as evidenced by increases in T_g , relative to its phenylene equivalent. As well, 1,4-naphthylene insertion appears to disrupt of chain packing since all the polymers appear amorphous by DSC. Decomposition temperatures of the dried polymers were measured in the range of 390 to 491 °C. Young's moduli varied from 0.39 GPa to 1.68 GPa.

1,4-Naphthylene insertion led to improvements in gas permselectivities for the BPA- and TMBP-derived polysulfones at the cost of lowering their permeabilities for various gases. This contradicts the objective of using the 1,4-naphthylene group in order to increase free volume and therefore improve the gas permeability of a polymer. Although there is no direct evidence regarding the effect of 1,4-naphthylene insertion on the free volume of the polymers in this thesis, it is obvious that the addition of the benzo unit, as in the case with 1,4-naphthylene incorporation, does not follow the same trend of aliphatic pendant groups as noted in section I.3. It seems reasonable to assume that the planar nature of the benzo group, relative to aliphatic groups (i.e. methyl), does not increase the free volume as effectively and therefore does not result in improvements to permeability. In fact, 1,4-naphthylene insertion is more effective in increasing in permselectivities, with minimal losses to permeabilities.

II.6. Experimental Section

Materials

4,4'-(Isopropylidene)diphenol (BPA), 4,4'-(hexafluoroisopropylidene)diphenol (6F-BPA) and 9,9-bis(4-hydroxyphenyl)fluorene (HFP) were recrystallized from toluene. 1,4-hydroquinone (HQ) was recrystallized from ethanol and bis(4-hydroxyphenyl)sulfone (BPS) from acetic acid. 2,2',6,6'-Tetramethyl-4,4'-biphenol (TMBP) was supplied by Dr. J. Roovers from the National Research Council and recrystallized from methanol. 1,2-Dihydro-4-(4-hydroxyphenyl)(2H)phthalazin-1-one was provided by Dalian University in China and used directly.

Reagent grade tetramethylene sulfone (TMSO₂) was fractionally distilled under vacuum (120°C/3 mmHg). Anhydrous potassium carbonate was grounded in a crucible before use. All other reagents phenolphthalein (PP), 4,4'-Biphenol (BP), AlCl₃, POCl₃, NaNO₂, CuCl, chlorobenzene, 1-amino-4-naphthalenesulfonic acid sodium salt hydrate, were purchased from the Aldrich Chemical Co. and used directly.

Measurements

The ¹H and ¹³C NMR spectra were recorded on the Bruker-400 instrument using tetramethylsilane as the internal reference. ¹⁹F NMR was recorded on a Varian XL-300 using CCl₃F as internal reference. Infrared measurements were performed on a Perkin-Elmer Series 1600 or a Bomem Michelson 120 FTIR spectrometer. KBr pellets were made for monomer IR samples and films were prepared for polymer IR samples. Low resolution mass spectra were obtained on a Du Pont 21-492B spectrometer. Apparent molecular weights were determined by gel permeation chromatography (GPC) using

chloroform at ambient temperature. Molecular weight calculations were based on polystyrene standards. A PL-Gel column (1.0 x 30 cm, 5 micron) with a chloroform elution flow rate of 1.0 mL/min was used. Elution of the polymers was detected by a Perkin-Elmer UV-vis spectrophotometric detector set at 254 nm. Inherent viscosities were measured in a 0.5 g/dL chloroform solution at 25°C using an Ubbelohde dilution viscometer. The glass transition temperatures were determined by differential scanning calorimetry (DSC) on a Seiko DSC 220 at a heating rate of 10°C/min under nitrogen (50 mL/min) and taken as the midpoint in the change in slope of the baseline. Thermogravimetric analysis (TGA) was performed on a Seiko TG/DTA 220 at a heating rate of 10°C/min in nitrogen (200 mL/min). Thin films for DMA study were cast from chloroform solution, dried from room temperature to 140 °C in 4 days under vacuum (1 mmHg), and cut into rectangular strips (length = 10 mm, width = 2 mm, thickness ~ 0.1 mm). Young's moduli (E') were recorded at 25 °C in static air with the following parameters: offset = 10-30 g, load = 5-15 g, amplitude = 5-10 g and cycling frequency = 0.05 - 0.2 Hz. Young's moduli were obtained from the average of the tangential slopes of the elliptical stress-strain plots.

Synthesis of 1-chloro-4-naphthalenesulfonyl chloride

The intermediate, 1-chloro-4-naphthalenesulfonic acid hydrate, was made from 1-amino-4-naphthalenesulfonic acid sodium salt hydrate based on the known procedure¹⁰

using the Sandmeyer reaction. A detailed procedure follows: A solution of NaNO_2 (31.0 g, 0.449 mole, 1.1 equiv.) and water (400 mL) was added to a purple solution of 4-amino-1-naphthalene sulfonic acid sodium salt hydrate (100.0 g, 0.408 mole, 1 equiv.) in 800 mL water. In a separate beaker, a solution of H_2SO_4 (160 mL concentrate) and 450 mL water was prepared. The amine/ NaNO_2 water solution was added to the aqueous H_2SO_4 solution which formed a yellow paste. After 20 minutes of stirring and monitoring with KI/starch solution, the excess nitrous acid was quenched with urea and the yellow paste was filtered. In another large beaker (4L), fresh CuCl (80.0 g, 0.810 mole, 2 equiv.) was added to chilled concentrate HCl (800 mL) to form a dark green solution. The yellow paste was added slowly to the CuCl/HCl solution with mechanical stirring. The reaction was slowly heated from 5°C to room temperature with bubbling evident at first. After stirring overnight (18 h) at room temperature, the solution was heated to 70°C for 8 h. The reaction was allowed to cool and then was filtered to form a grey powder. The product was rinsed thoroughly with water, then diethyl ether and dried for two days (room temperature, 40 mmHg). Yield 93.4 g (88%).

Phosphorus oxychloride (POCl_3) (360 mL, 3.88 mole, 9.5 equiv.) was then added slowly to the above product in a three-necked round bottomed flask, previously cooled by an ice bath, using a mechanical stirrer. As the bubbling subsided, the flask was allowed to warm to room temperature, then heated at 110°C over two days. The reaction was then quenched by pouring it *slowly* into a large bucket containing crushed ice (4L). *Careful! POCl_3 reacts violently with water!* The melted ice/product solution was filtered to give a grey powder and aqua blue colored filtrate. The product was air dried overnight before

recrystallizing with petroleum ether (600 mL) to give 1-chloro-4-naphthalenesulfonyl chloride. Yield: 37% (39 g); m.p. 95-97 °C (lit. m.p. 92-93 °C)¹⁰; IR (KBr): 1374 and 1167 cm⁻¹ (S=O asymmetric and symmetric stretch); MS (EI, *m/z*, relative intensity %): 260 (*M*⁺ - Cl, 21.8), 161 (*M*⁺ - SO₂Cl, 100.0); ¹H NMR(400 MHz, CDCl₃) δ 8.85 (d, 1H, ³J_{H-H} = 8.8 Hz) 8.47 (d, 1H, ³J_{H-H} = 8.4 Hz), 8.28 (d, 1H, ³J_{H-H} = 8.1 Hz), 7.85 (m, 2H), 7.71 (d, 1H, ³J_{H-H} = 8.1 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 141.82, 138.63, 131.90, 130.47, 129.39, 129.07, 128.65, 126.12, 124.88, 124.73.

Synthesis of (4-chloronaphthalene)(4-fluorobenzene)sulfone

Fluorobenzene (10 mol equiv.) was added to 1-chloro-4-naphthalenesulfonyl chloride (19.6 g, 0.075 mole, 1.0 equiv.) in a reaction flask cooled by an ice bath. Anhydrous AlCl₃ (10.5 g, 0.0825 mole, 1.1 equiv.) was added slowly and the reaction mixture stirred for 1 hour at 0°C. The temperature was then increased to 80 °C and held at this temperature for 3 h. The reaction was quenched by addition to iced-water containing a few drops of concentrated HCl. The product was then extracted into dichloromethane and washed successively with 5% aqueous NaOH, brine and distilled water. The organic layer was dried with MgSO₄, filtered and evaporated down to give a sticky product. Recrystallization twice in toluene gave (4-chloronaphthalene)(4-fluorobenzene)sulfone as colorless crystals. Yield: 16.9 g (70.1%). m.p. 196-199 °C; IR (KBr) 1318 and 1140 cm⁻¹ (S=O asymmetric and symmetric stretch); MS (EI, *m/e*, relative

intensity %) 320 (M^+ , 89.6), 221 (M^+ -PhF, 100.0), 161 (Cl-naph $^+$, 33.7), 126 (naph $^+$, 88.2); UV/VIS ($CHCl_3$): λ/nm 241.5, 302.8; 1H NMR (400 MHz, $CDCl_3$) δ 8.65 (m, 1H), 8.43 (d, 1H, $^3J_{H-H} = 8.0$ Hz), 8.36 (m, 1H), 7.96 (dd, 2H, $^3J_{H-H} = 8.5$ Hz, $^4J_{H-F} = 5.0$ Hz), 7.72 (d, 1H, $^3J_{H-H} = 8.0$ Hz), 7.65 (m, 2H), 7.14 (dd, 2H, $^3J_{H-H} = 8.5$ Hz, $^3J_{H-F} = 8.5$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.39 ($^1J_{C-F} = 255$ Hz), 139.62, 137.64 ($^4J_{C-F} = 4$ Hz), 134.92, 131.47, 130.26 ($^3J_{C-F} = 9$ Hz), 129.77, 129.41, 129.23, 128.08, 125.71, 124.99, 124.66, 116.58 ($^2J_{C-F} = 23$ Hz); ^{19}F NMR (300 MHz) δ -104.38 (s, 1F).

Polymerizations

All the polymerizations were done as follows: A bisphenol and monomer **II-1** (3.0 mmol each) were dissolved in tetramethylene sulfone in 40% (w/v) solid content. An equivalent volume of chlorobenzene and anhydrous K_2CO_3 (0.746 g, 5.4 mmol) were then added. The reaction mixture was heated under nitrogen from room temperature to 200 °C in 30 min. The chlorobenzene and the formed water were codistilled off. The polymerization was monitored by GPC and stopped when the molecular weight failed to increase. If the reaction mixture became too viscous to stir, it was diluted with tetramethylene sulfone (2 mL). The polymer was isolated by precipitation in methanol. All polymers were purified by dissolving in chloroform (~100 mL)(except for polymer **II-3e** which were dissolved TCE) and filtering through Celite to remove salts. Lower molecular weight fractions were observed in all the polymers on the GPC profile. Reverse precipitation was done on all the polymers except polymer **II-3e** to remove these fractions. Molecular weights were taken of the reprecipitated products and recorded in Table II.3.

Reverse precipitation involved adding methanol dropwise into the Celite purified chloroform (or TCE) polymer solution. This coagulated to form a gummy residue and a white cloudy solution consisting of the lower molecular weight fractions. The cloudy solution was then decanted and the gummy residue was dissolved in chloroform, or TCE (~20 mL) and precipitated into methanol (~200 mL) to form white fibrous material.

Polymer II-3a: Yield: 1.41 g, (95%); IR (film, cm^{-1}): 1244 (S=O), 1147 (S=O); UV/VIS (CHCl_3) λ_{nm} 241.2, 311.7; ^1H NMR (400 MHz, CDCl_3): δ 8.63 (d, 1H, $J_{\text{H-H}} = 8.3$ Hz), 8.44 (m, 1H), 8.35 (m, 1H), 7.87 (m, 2H), 7.58 (m, 2H), 7.28 (m, 4H), 7.05 (m, 2H), 6.93 (m, 4H), 6.80 (m, 1H), 1.75-1.66 (3s, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 162.06, 159.86, 153.18, 153.05, 147.77, 147.41, 135.84, 131.39, 130.31, 129.79, 129.59, 128.6, 128.88, 128.69, 126.92, 126.73, 124.62, 123.32, 120.54, 120.11, 117.74, 42.77, 42.75, 42.73, 31.28.

Polymer II-3b: Yield 1.60 g (89%); IR (film, cm^{-1}): 1246 (S=O), 1149 (S=O); UV/VIS (CHCl_3) λ_{nm} 241.5, 306.7; ^1H NMR (400 MHz, CDCl_3): δ 8.69 (d, 1H, $J = 8.7$ Hz), 8.40 (m, 2H), 7.95 (m, 2H), 7.65 (m, 2H), 7.45 (m, 4H), 7.15 (m, 2H), 7.01 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3): δ 160.54, 158.31, 156.25, 156.00, 136.71, 132.25, 132.08, 131.04, 130.62, 130.22, 129.78, 129.63, 129.30, 127.05, 126.87, 125.55, 124.51, 122.98, 122.70, 119.70, 119.30, 118.62, 118.60, 109.68.

Polymer **II-3c**: Yield: 1.35 g (91%); IR (film, cm^{-1}): 1241 (S=O), 1145 (S=O); UV/VIS (CHCl_3) λ/nm 242.1, 265.2, 310.8; ^1H NMR (400 MHz, CDCl_3): δ 8.68 (m, 1H), 8.48 (m, 1H), 8.40 (m, 1H), 7.93 (m, 2H), 7.61 (m, 6H), 7.23 (m, 2H), 7.04 (m, 4H), 6.88 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 161.46, 159.23, 154.05, 154.01, 153.89, 153.85, 150.81, 142.69, 142.31, 140.07, 135.83, 131.04, 130.06, 129.94, 129.90, 129.78, 129.65, 129.51, 129.04, 127.95, 127.91, 127.87, 126.67, 126.52, 126.02, 124.36, 122.97, 120.43, 120.36, 119.94, 119.90, 117.69, 108.27.

Polymer **II-3d**: Yield: 1.35g (89 %); IR (film, cm^{-1}) 1235 (S=O), 1146 (S=O); UV/VIS (CHCl_3) λ/nm 265.56, 308.33; ^1H NMR (400 MHz, CDCl_3): δ 8.65 (m, 2H), 8.32 (m, 1H), 7.89 (m, 2H), 7.66 (m, 2H), 7.42-7.29 (4s, 4H), 6.87 (m, 2H), 6.51 (m, 1H), 2.10-2.22 (4s, 12H); ^{13}C NMR (100 MHz, CDCl_3): δ 161.35, 158.27, 150.07, 150.02, 149.88, 149.83, 138.24, 138.03, 134.96, 131.37, 131.32, 130.27, 129.82, 128.94, 128.05, 127.99, 127.92, 127.87, 126.56, 125.53, 124.57, 123.0, 115.15, 104.66, 16.47, 16.45, 16.32, 16.30.

Polymer **II-3e**: Yield: 1.09 g (71%); IR (film, cm^{-1}): 1241(S=O), 1146 (S=O); UV/VIS (CHCl_3) λ (nm) 241.02, 259.9, 306.1; ^1H NMR (400 MHz, DMSO-d_6): δ 8.60 (d, 1H), 8.39 (d, 1H), 8.32 (m, 1H), 7.98 (m, 6H), 7.72 (m, 1H), 7.36 (m, 1H), 7.20 (m, 5H); ^{13}C NMR (50 MHz, DMSO-d_6): δ 160.73, 160.31, 160.22, 157.54, 137.83, 137.63, 137.46, 132.40, 131.94, 131.19, 131.70, 130.23, 128.50, 127.21, 125.01, 123.52, 121.05, 121.64, 113.12.

Polymer **II-3f**: Yield: 0.97 g (87%); IR (film, cm^{-1}): 1235 (S=O), 1145 (S=O); UV/VIS (CHCl_3) λ/nm 241.5, 259.9, 306.1; ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 8.58 (m, 1H), 8.37 (m, 2H), 7.93 (m, 2H), 7.70 (m, 2H), 7.11 (m, 7H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 161.30, 158.73, 151.55, 151.35, 151.30, 151.10, 135.08, 131.26, 129.61, 129.32, 129.11, 127.06, 125.45, 123.79, 122.69, 122.54, 122.37, 122.22, 117.38, 108.28.

Polymer **II-3g**: Yield: 1.78 g (98%); IR (film, cm^{-1}): 1242 (S=O), 1146 (S=O); UV/VIS (CHCl_3) λ/nm 241.5, 264.0, 309.1; ^1H NMR (400 MHz, CDCl_3): δ 8.59 (m, 1H), 8.36 (m, 1H), 8.30 (m, 1H), 7.81 (m, 2H), 7.77 (m, 2H), 7.55 (m, 2H), 7.30 (m, 10H), 6.95 (m, 4H), 6.75 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 161.45, 159.23, 154.05, 154.01, 153.89, 153.85, 150.81, 142.69, 142.31, 140.07, 135.83, 131.04, 130.06, 129.94, 129.90, 129.78, 129.74, 129.65, 129.51, 129.04, 127.95, 127.91, 127.87, 126.67, 126.52, 126.02, 124.36, 122.97, 120.43, 120.36, 120.31, 119.94, 119.90, 117.69, 108.27, 64.54.

Polymer **II-3h**: Yield: 1.52 g (87%); IR (film, cm^{-1}) 1771 (C=O), 1243 (S=O), 1146 (S=O); UV/VIS (CHCl_3) λ/nm 268.61, 308.33; ^1H NMR (400 MHz, CDCl_3): δ 8.61 (m, 1H), 8.34 (m, 2H), 7.95 (m, 1H), 7.85 (m, 2H), 7.73 (m, 1H), 7.56 (m, 4H), 7.36 (m, 4H), 7.08 (m, 2H), 6.95 (m, 4H), 6.82 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.30, 161.00, 158.73, 155.74, 155.71, 155.50, 155.46, 151.58, 137.44, 137.12, 136.23, 134.50, 130.97, 130.16, 130.09, 129.77, 129.65, 129.2, 129.07, 129.02, 126.90, 126.63, 126.31, 125.47, 124.39, 124.00, 122.94, 120.34, 120.00, 118.09, 108.99, 90.73.

Polymer II-3i: Made by Jeff Franklin: Yield 84%; IR (film, cm^{-1}): 1671 (C=O), 1325 (S=O), 1144 (C-O); UV/VIS (CHCl_3) λ 268.61 nm, 308.33 nm.

Preparation of polysulfone membranes for gas permeation study

The polymer film was cast from a 2% (wt/wt) chloroform solution to form a 100 μm thick circular membrane. Chloroform was allowed to evaporate slowly (1.5 d) in an atmosphere until the film was tack free. Then while under vacuum, the membrane was heated slowly to above its glass transition temperature and the polymer was annealed.

Gas Permeation Studies

Gas permeability can be expressed as the flux of a gas, Q , which is normalized for variables such as film thickness (l), its surface area (A) and the pressure difference across the film (Δp) i.e. $P = \frac{Q \cdot l}{A \cdot \Delta p}$

$$A \cdot \Delta p$$

Permeabilities were measured using a constant volume system as described in Pierre Moulinie's Ph. D. Thesis. 1996, Carleton University. Nitrogen, oxygen, methane and carbon monoxide (all in ultra high purity, available from Canox) were used individually, in the above order, as the penetrant gases and were permeated from the upstream side at 150 psi. Gas permeated to the downstream side of a polymer film sealed tightly in a permeation cell. The downstream side was connected to a 100 mmHg pressure transducer and vacuum. The volumetric flux can therefore be calculated from the pressure increase of the downstream side. Permeability is expressed in units of Barrer:

$$1 \text{ Barrer} = \frac{(\text{cm}^3 / \text{sec}) \cdot \text{cm}}{\text{cm}^2 \cdot \text{cmHg}} \times 10^{10}$$

Downstream pressure vs. time data was collected. The time lag, θ , is the time required for the gas to achieve a 'steady state'. From the pressure versus time plot, the slope is calculated from 3θ to 6θ . From this slope, and using the ideal gas law, the volumetric flux can be calculated and substituted into the above equation to give the permeability of the polymer.

II.7. References

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III.1. Introduction

Poly(aryl ether ketone)s, or PAEK, make up an important class of poly(aryl ether)s.¹ Poly(aryl ether ketone)s are typically strong rigid materials with outstanding heat resistance and can display crystalline behaviour. Applications of PAEK include coatings for high performance wiring in aeronautics and advanced structural composites. An important commercial example is poly(ether ether ketone), or PEEK, whose chemical structure is shown in Figure III.1.² PEEK has a T_g of 143 °C and T_m of 334 °C.²

Figure III.1. PEEKTM

The insertion of a 1,4-naphthylene group was proposed in chapter one as a means to disrupt chain packing, improve processability, enhance gas transport properties and increase thermal stability. The incorporation of the 1,4-naphthylene unit was accomplished through the design and synthesis of a unique series of unsymmetric dihaloarylketone monomers **III-1(a-d)** as outlined in Scheme III.1.

Chapter one showed that a monomer containing the 1,4-naphthylene group provided greater stabilization to the Meisenheimer intermediate through its many resonance structures, therefore will be more reactive towards nucleophilic substitution. Hückel molecular orbital (HMO) calculations were performed to evaluate the reactivity of the target monomer.³ 4,4'-Dichlorobenzophenone and 4,4'-difluorobenzophenone have net charge densities of 0.025 and 0.050, respectively, on the carbon atoms attached to the halogen atoms (Figure III.2).

Figure III.2. Charge densities of symmetric dihaloaryl ketone monomers

HMO calculations performed on the proposed unsymmetric monomers **III-1(a-d)** suggest that the chloronaphthyl ring is indeed more reactive than the chlorophenyl unit towards nucleophilic displacement (Figure III.3). The net charge densities of the naphthyl carbon attached to the chlorine atom in monomers **III-1b** and **III-1d** are 0.044 and 0.045, respectively. The phenyl chloride in both **III-1c** and **III-1d** do not appear reactive enough with net charge densities of 0.021 and 0.023. These calculations, although not always accurate, indicate the increased aptitude the 1,4-naphthylene ring has to displace chlorine over the 1,4-phenylene ring.

Figure III.3. Charge densities of proposed monomers **III-1(a-d)**

The ketone monomers **III-1(a-d)** were polymerized with selected bisphenols in order to evaluate their relative reactivities. Copolymerizations and model reactions were performed in order to further probe the reactivity of the dihalide aryl monomers. Monomer **III-1b** was polymerized the eight different bisphenols and one heterocyclic monomer to obtain a new series of PAEK containing the 1,4-naphthylene moiety.

II.2. Monomer Syntheses

III.2.1. Synthesis

The four proposed dihalobenzonaphthones were synthesized by the Friedel-Crafts reaction of 4-chloro- and 4-fluorobenzoyl chlorides with 1-chloro- and 1-fluoronaphthalenes (Scheme III.1).⁴ Modest yields were obtained for **III-1a**, **III-1b** and **III-1c**, (71%, 63% and 63% respectively). A poor yield of 14% prevailed after several attempts to synthesize **III-1d**. The poor yield can be explained by the presence of several isomers as seen by TLC. Although not identified, anticipated isomers included: (a) *ortho* substitution since chlorine and fluorine are both *ortho*- and *para*- directors in electrophilic substitutions,⁵ (b) acyl substitution on the 'bottom' ring of the naphthylene moiety⁶ and (c) isomerization of the halogen from the 1-naphthyl to 2-naphthyl position.⁶ In fact, 1-chloronaphthalene is known to isomerize to 2-chloronaphthalene in Friedel-Crafts reactions more readily than 1-fluoronaphthalene.⁶ Therefore the poor yield of **III-1d** seems justified. In all cases, isomers were successfully removed by recrystallization.

Scheme III.1. Syntheses of ketone monomers **III-1(a-d)**⁴

III.2.2. Characterization

MS, IR and detailed analyses of ^1H , ^{13}C and ^{19}F NMR spectra confirmed the structures of all four ketone monomers. MS indicated molecular ion peaks of 268, 284, 284 and 300 for **III-1a**, **III-1b**, **III-1c** and **III-1d** respectively. MS displayed fragmentation patterns appropriate for each monomer. IR showed carbonyl stretching frequencies at 1657 cm^{-1} and 1656 cm^{-1} for the fluorobenzoyl-containing monomers **III-1a** and **III-1b**. The chlorobenzoyl-based **III-1c** and **III-1d** monomers both displayed a ketone peak at 1645 cm^{-1} .

The ^1H NMR spectra of **III-1a** and **III-1b** are displayed in Figure III.4 and the ^1H NMR spectra of **III-1c** and **III-1d** are shown in Figure III.5. Assignments were made based on COSY experiments. The internal proton, Hg, appeared furthest deshielded for each monomer ($\sim 8.2\text{ ppm}$ to 8.4 ppm). Doublets could be seen for the Ha ($\sim 7.5\text{ ppm}$) and Hb ($\sim 7.8\text{ ppm}$) protons on the chlorophenyl units of **III-1c** ($^3J_{\text{H-H}} = 8.4\text{ Hz}$) and **III-1d** ($^3J_{\text{H-H}} = 8.8\text{ Hz}$). Doublets appeared at $\sim 7.6\text{ ppm}$ and $\sim 7.5\text{ ppm}$ for the Hc and Hd protons, respectively, on the chloronaphthyl moiety ($^3J_{\text{H-H}} = 7.6\text{ Hz}$) of **III-1b** and **III-1d**. Hg and Hh showed fine splitting patterns on the chloronaphthyl part.

Additional splitting was observed due the presence of fluorine atoms. A triplet was seen upfield ($\sim 7.14\text{ ppm}$) for the proton labeled Ha on the fluorobenzoyl portion of **III-1a** and **III-1b** which is split equally by Hb ($^3J_{\text{H-H}} = 8.8\text{ Hz}$) and by fluorine ($^3J_{\text{H-F}} = 8.8\text{ Hz}$). The Hb proton appeared further downfield ($\sim 7.8\text{ ppm}$), for both **III-1a** and **III-1b**, as a doublet of doublets due to splitting by the neighbouring proton Ha and the longer range splitting by fluorine and ($^3J_{\text{H-H}} = 8.8\text{ Hz}$ and $^4J_{\text{H-F}} = 5.6\text{ Hz}$). The Hc proton of the fluoronaphthyl portion of **III-1a** and **III-1c** displayed similar splitting as Hb (doublet of

Figure III.4. The 400 MHz ^1H NMR spectra (6.8 to 8.6 ppm) of ketone monomers **III-1a** and **III-1b**

Figure III.5. The 400 MHz ^1H NMR spectra (7.0 to 8.3 ppm) of ketone monomers **III-1c** and **III-1d**

doublets at ~ 7.5 ppm, $^3J_{\text{H-H}} = 8.0$ Hz and $^4J_{\text{H-F}} = 5.6$ Hz) due to the neighbouring Hd and further range fluorine. Interestingly, the Hd proton of the same ring appeared as a doublet of doublets (~ 7.2 ppm for each) rather than the expected triplet. Calculations reveal Hd is not split equally by the neighbouring fluorine atom and Hc proton ($^3J_{\text{H-H}} = 8.0$ Hz and $^4J_{\text{H-F}} = 10.0$ Hz). This is felt to be reflective of the naphthalene ring.

Calculations of ^1H and ^{13}C NMR chemical shifts were made based on structures given in Figure III.6.⁷ Comparisons of the calculated ^1H NMR chemical shifts with experimental values are given in Table III.1. Good correlation exists for the phenylene moieties of all four monomers and only slightly deviated when the naphthylene ring was approximated by the phenylene ring. It was not possible to calculate chemical shifts of protons on the bottom ring of the naphthalene moiety.

Figure III.6. 4-Chlorobenzoyl and 4'-fluorobenzoyl moieties used in NMR calculations

Table III.1. Comparison of Estimated and Experimental ^1H NMR Chemical Shifts

Monomer	Phenyl Naphthyl	4-Chlorobenzoyl		4'-fluorobenzoyl	
		Ha	Hb	Ha'	Hb'
Estimated	Phenyl	7.49	7.77	7.17	7.77
III-1a (exptl)	Phenyl	-	-	7.14 (t)	7.88 (dd)
	Naphthyl	-	-	7.17 (dd)	7.46 (dd)
III-1b (exptl)	Phenyl	-	-	7.13 (t)	7.88 (dd)
	Naphthyl	7.47 (d)	7.63 (d)	-	-
III-1c (exptl)	Phenyl	7.45 (d)	7.79 (d)	-	-
	Naphthyl	-	-	7.17 (dd)	7.55 (dd)
III-1d (exptl)	Phenyl	7.47 (d)	7.79 (d)	-	-
	Naphthyl	7.49 (d)	7.63 (d)	-	-

The ^{13}C NMR data are reported in the experimental section. HETCOR, in combination with COSY experiments, aided in the assignment of most carbon atoms. Key peaks are identified in Table III.2 and compared to their calculated values. Correlation of experimental to estimated results seemed reasonable. Additional splitting is evident due to the presence of fluorine atoms. Coupling constants for the carbon attached to the fluorine atom were ~ 250 Hz ($^1J_{\text{C-F}}$), ~ 30 Hz for the *ortho* carbon ($^2J_{\text{C-C}}$) and ~ 10 Hz for the *meta* carbon ($^3J_{\text{C-C}}$).

Table III.2. Comparison of Estimated and Experimental C^{13} NMR Chemical Shifts.

Monomer	Phenyl or Naphthyl	4-Chlorobenzoyl		4'-Fluorobenzoyl	
		C-2	C-3	C-2'	C-3'
Calculated	Phenyl	128.7	131.3	115.4	129.0
III-1a (exptl)	Phenyl	-	-	115.7	133.0
	Naphthyl	-	-	108.2	128.8
III-1b (exptl)	Phenyl	-	-	116.4	133.6
	Naphthyl	128.6	126.6	-	-
III-1c (exptl)	Phenyl	128.8	131.7	-	-
	Naphthyl	-	-	108.2	129.1
III-1d (exptl)	Phenyl	128.6	131.4	-	-
	Naphthyl	127.1	124.5	-	-

The ^{19}F NMR spectrum showed sharp, singlet peaks for all three monomers bearing fluorine atoms, **III-1(a-c)**, establishing the purity of the monomers, in light of potential isomer formation. ^{19}F NMR can also provide insight into monomer reactivity due to its ability to measure the electronic density at the site of nucleophilic reaction.⁸ 4,4'-difluorobenzophenone has a peak at -106.0 ppm.⁹ The fluorophenyl moieties of **III-1a** and **III-1b** showed peaks at -104.9 ppm and -104.3 ppm, indicating their sufficient

activities towards nucleophilic displacement. The ^{19}F NMR spectrum displayed peaks at -117.2 ppm and -116.8 ppm for the fluoronaphthyl portions of **III-1a** and **III-1c**. This implied that a greater net charge exists at the carbon bearing the fluorine atom on the naphthyl ring than on the phenyl ring. Model studies were conducted to explore the perceived ability that naphthyl rings can enhance the reactivity of halogens towards nucleophilic displacement.

III.3. Polymerization of Four Dihaloaryl Monomers

III.3.1. Solvent Effects

There are many dipolar aprotic solvents which can be used to polymerize poly(aryl ether)s.¹⁰ Two solvent systems were investigated in order to determine which would be best suited for the polymerization of this series of monomers.^{4c}

The first one involved NMP with toluene as the azeotroping solvent in a 20% solid content at 180 °C (Table III.3). It was possible to make high molecular weight polymers from **III-1a** with both BPA and HQ ($M_w = 13.8 \times 10^4$ and 7.63×10^4 respectively). But difficulties arose when trying to polymerize **III-1b** with BPA ($M_w = 3.64 \times 10^4$). A modest molecular weight of 3.64×10^4 ($\eta_{inh} = 0.36$ dL/g) was obtained in NMP. A dark green color was also observed in the reaction mixture. Strukelj *et al.* studied the solvent effects in the preparation of poly(aryl ether benzils)s and suggested that the green color stems from impurities in the commercially available NMP.¹¹ Decomposition products of NMP or reactions of reactive species with NMP, also seem to have a dramatic effect on molecular weight and appear to degrade the polymer after molecular weight build-up. Percec *et al.* also observed that reductive dehalogenation of diaryl halides can occur in NMP.¹²

In an effort to avoid these problems and increase molecular weight, a second solvent system, TMSO₂ and chlorobenzene, was used. A better result was obtained for polymerization of **III-1b** and BPA ($M_w = 10.86 \times 10^4$; $\eta_{inh} = 0.58$ dL/g) at 210 °C in a 35% solid content when using this alternative solvent system (Table III.4). Therefore,

TMSO₂ and chlorobenzene was chosen as the preferred polymerization solvent system in the rest of the studies.

Table III.3. Polymerization of BPA and HQ with **III-1a** and **III-1b** in NMP.

Monomer	Bisphenol	$M_w \times 10^{-4}$	$M_n \times 10^{-4}$	M_w/M_n	η_{inh} (dL/g)
III-1a	BPA	13.8	6.68	2.06	0.73
III-1a	HQ	7.63	3.89	1.96	0.57
III-1b	BPA	3.64	2.14	1.70	0.36
III-1b	HQ	8.09	3.79	2.13	0.54

III.3.2. Polymerization of Four Dihaloaryl Monomers.

All four monomers, **III-1(a-d)**, were polymerized with BPA, 6F-BPA, HQ and HFP in order to compare the polymerizability of each monomer (Scheme III.2).

Scheme III.2. Polymerization of monomers **III-1(a-d)** to form PAEK **III-(2-5)**

Molecular weights and inherent viscosities are reported in Table III.3. Among several factors which govern the success of polycondensations between dihaloaryl monomers and bisphenols, the reactivity and chemical specificity of the pair of monomers are of utmost importance. It was found that high molecular weight polymers could be made with all four monomers except for **III-1c** and **III-1d** with BPA ($M_w = 3.67 \times 10^4$ and $M_w = 3.98 \times 10^4$). BPA proved to be more discriminating amongst the bisphenols when reacting with the four dihalobenzoyl naphthones to make a polymer.

Both **III-1c** and **III-1d** contain the 4-chlorobenzoyl moiety which has been reportedly difficult to polymerize with BPA.¹² The monomers, **III-1a** and **III-1b**, contain the undoubtedly reactive 4-fluorobenzoyl moiety. In addition, the polymerizable **III-1b** monomer contains the chloronaphthyl group. Thus the naphthyl ring appears to promote chlorine displacement in polyetherifications with bisphenoxides relative to the phenyl ring.⁴ The enhanced reactivity can be attributed to the increased conjugation and stability imparted to the Meisenheimer complex by the naphthylene ring as predicted in the introduction. This also corroborates HMO calculations which show a greater net density charge exists on the carbon bearing the chlorine atom on the naphthylene ring than on the phenylene ring.

Table III.3. Molecular Weights and Inherent Viscosities of PAEK III-(2-5)

Polymer	Dihalide	Bisphenol	M_w $\times 10^{-4}$	M_n $\times 10^{-4}$	M_w/M_n	η_{inh} (dL/g)
2	III-1a	BPA	16.0	5.70	2.80	0.90
2	III-1b	BPA	10.9	4.12	2.64	0.58
2	III-1c	BPA	3.67	1.88	1.95	0.28
2	III-1d	BPA	3.98	2.23	1.76	0.27
3	III-1a	6F-BPA	16.9	9.10	1.86	0.84
3	III-1b	6F-BPA	11.6	4.95	2.35	0.73
3	III-1c	6F-BPA	6.00	1.96	3.05	0.43
3	III-1d	6F-BPA	12.4	6.26	1.98	0.65
4	III-1a	HQ	7.20	2.26	3.19	0.61
4	III-1b	HQ	6.05	2.30	2.63	0.60
4	III-1c	HQ	6.73	2.66	2.53	0.56
4	III-1d	HQ	6.03	2.25	2.68	0.55
5	III-1a	HFP	18.8	10.0	1.88	0.76
5	III-1b	HFP	20.2	9.89	2.05	0.86
5	III-1c	HFP	11.9	5.15	2.30	0.55
5	III-1d	HFP	13.4	3.72	3.59	0.66

III.3.3. Copolymerization

In an effort to minimize the amount of expensive difluoro monomer **III-1a** used in polycondensation, several copolymerizations were done in molar ratios of 1:1, 1:2, 1:4 and 1:9 of **III-1a** to **III-1d** with BPA (Table III.5). Reasonably high molecular weights were achieved with ratios of **III-1a** to **III-1d** as low as 1 to 4 ($M_w = 4.97 \times 10^4$, Table III.5) in comparison with polymerization of 100% **III-1d** and BPA ($M_w = 3.98 \times 10^4$, Table III.4). In light of these results, a halogen exchange reaction between the chlorine on the phenyl part with *in-situ* generated fluoride ion during polycondensation seemed possible. Therefore, two model reactions were performed to investigate this phenomenon.

Table III.5. Copolymerization of Monomers **III-1a** and **III-1d** with BPA

Molar Ratio III-1a : III-1d	$M_w \times 10^{-4}$	$M_n \times 10^{-4}$	M_w/M_n	η_{inh} (dL/g)
1:1	10.6	5.40	1.96	0.55
1:2	6.18	2.89	2.14	0.44
1:4	4.97	2.68	1.86	0.37
1:9	4.62	2.16	2.14	0.29

III.3.4. Model Reactions to Study *In-Situ* Halogen Exchange Reaction

In order to investigate the possibility of an *in-situ* halogen exchange reaction, the following two model studies were done. In the first model reaction, monomer **III-1d** was subjected to standard polymerization conditions (210 °C, TMSO₂/PhCl and K₂CO₃) without a bisphenol but with KF to promote the halogen exchange of chlorine with fluorine (Scheme III.3). It was found that **III-1b** formed faster and in a greater yield than **III-1c** (Figure III.7). This demonstrated that the Cl-F exchange occurs more rapidly on the phenylene ring than on the naphthylene ring. A halogen exchange of this kind would facilitate polymerization.

Scheme III.3. Model Cl-F exchange reaction using KF

And yet this seems to contradict earlier findings that the chloronaphthyl portion of the monomer is more reactive to nucleophilic displacement. Why the difference?

Halogen Exchange	Polymerization
$\text{-Naph-Cl} + \text{F}^- \xrightarrow{\text{Slow}} \text{-Naph-F}$	$\text{-Naph-Cl} + \text{ArO}^- \xrightarrow{\text{Fast}} \text{-Naph-O-Ar}$
$\text{-Ph-Cl} + \text{F}^- \xrightarrow{\text{Fast}} \text{-Ph-F}$	$\text{-Ph-Cl} + \text{ArO}^- \xrightarrow{\text{Slow}} \text{-Ph-O-Ar}$

According to the 'hard acid soft base theory' (HASB),¹³ hard acids prefer to react with hard bases and soft acids prefer to react with soft bases. 'Soft' implies that the species is highly polarizable, 'hard' means that it has low polarizability.¹³ By definition, the fluoride anion is a hard base and the phenoxide anion is a soft base. It would follow that the chloronaphthyl portion is a 'softer' acid than the chlorophenyl part because it can delocalize the charge more effectively. The hard acid, the chlorophenyl part, would then prefer to react with a hard base like the fluoride. And the soft acid, the chloronaphthyl portion, would prefer to react with the phenoxide anion. The HASB theory therefore explains the apparent discrepancy between the two reactivities of the halogen exchange and polymerization.

A second model reaction was done in which fluoride ion was generated *in-situ* by reacting two equivalents of phenol with **III-1a** (Scheme III.4). Monomer **III-1d** was then added to the reaction mixture to see if any Cl-F exchange occurred. Using the *in-situ* generated fluoride ion was believed to be closer to the actual polymerization environment than the addition of KF salt. It was discovered that **III-1b** was formed in greater quantity than **III-1c** but at a much slower rate than in the first model reaction (Figure III.8). Although being confirmed, this slow halogen exchange perhaps plays a minor role in the actual polymerization mechanism.

Scheme III.4. *In-situ* Cl-F exchange model reaction

Figure III.7. Model Cl-F exchange reaction using KF

Figure III.8. *In-situ* Cl-F exchange model reaction

III.3.5. End-Capping

End-capping controls the molecular weight and allows one to calculate an absolute molecular weight as opposed to an apparent molecular weight as GPC provides. Thus an end-capping experiment was carried out in order to evaluate the accuracy of the molecular weight values given by GPC for this family of poly(aryl ether ketone)s.

The end-capping experiment was carried out with a 1% excess of the difluoride monomer **III-1a** and 2% of 3,5-di-*tert*-butylphenol relative to BPA. From the high resolution ^1H NMR spectrum, the relative integration values of the aliphatic peaks at 1.6 ppm (the methyl groups of BPA) and 1.3 ppm (*tert*-butyl groups) were calculated and the number of repeat units (n) was found to be 127 (Figure III.9). Accordingly, the number-average molecular weight (M_n) was calculated to be 58,300 which is larger than that obtained by GPC ($M_n = 47,300$). And yet, one would expect GPC to overestimate the molecular weight of the PAEK because of its larger size relative to the polystyrene standard. The discrepancy is believed to be due to the error associated with NMR. The inherent viscosity (η_{inh}) for the end-capped polymer was found to be 0.47 dL/g.

Figure III.9. ¹H NMR spectrum (6.5 to 8.5 ppm; 1.4 to 1.7 ppm) of end-capped BPA-based PAEK

III.4. Polymerization of 4'-Chloro-4-Fluorobenzo-1'-Naphthone

The monomer, 4'-chloro-4-fluorobenzo-1'-naphthone (**III-1b**), was chosen to complete the series of unsymmetric naphthalene-containing polymers due to its relative low cost, yet effective reactivity. Polycondensation of **III-1b** with BP, TMBP, BPS, PP and PZ was conducted at 210 °C using $\text{TMSO}_2/\text{PhCl}$ and K_2CO_3 .^{4,14} Scheme III.5 shows the structures of BPA, 6F-BPA, HQ and HFP for easy comparison.

Scheme III.5. Polymerization of **III-1b** to form PAEK **III-6(a-i)**

III.4.1. Molecular Weights and Solubilities

Molecular weights, as determined by GPC, and inherent viscosities are reported in Table III.6. Molecular weights and inherent viscosities of PAEK made from **III-1b** and

BPA, 6F-BPA, HQ and HFP are included in Table III.6. for easy comparison. High molecular weight polymers were achieved with all bisphenols except BPS. The low reactivity of BPS is symptomatic of the electron withdrawing sulfone unit in BPS. The equivalent polysulfone in chapter two resulted in a low molecular weight polymer as well.

Table III.6. Molecular Weights and Inherent Viscosities of PAEK III-6(a-i)

PAEK	Bisphenol	$M_w^a \times 10^{-4}$	$M_n^a \times 10^{-4}$	M_w/M_n	η_{inh}^b (dL/g)
III-6a	BPA	10.90	4.12	2.64	0.58
III-6b	6F-BPA	11.6	4.95	2.35	0.73
III-6c	BP	15.4	8.46	1.82	0.56
III-6d	TMBP	5.02	2.07	2.42	0.76
III-6e ^d	BPS	1.01	0.62	1.63	n/a ^c
III-6f	HQ	6.05	2.30	2.63	0.60
III-6g	HBP	20.2	9.89	2.05	0.86
III-6h	PP	22.9	11.51	1.99	0.70
III-6i	PZ	4.36	2.07	2.11	0.29

^a Taken by GPC relative to polystyrene standards.

^b Inherent viscosity, 0.5 % chloroform solution at 25.0 °C.

^c not obtained due to low molecular weight.

^d polymerization attempted three times.

All the polymers were soluble in chloroform, TCE and NMP (Table III.7). All could form tough, flexible films from chloroform solution except III-6e. The BPS-based polymer was not characterized further. Most were soluble in dichloromethane except the

BP and TMBP-based ones (**III-6c** and **III-6d**). Most polymers were only partially soluble in DMF with the exception of the BPS and PP-derived ones (**III-6e** and **III-6h**).

Table III.7. Solubilities of PAEK **III-6(a-i)**^a

Polymer	CHCl ₃	TCE	CH ₂ Cl ₂	NMP	THF	DMF	DMAc
III-6a	+	+	+	+	+	+/-	+
III-6b	+	+	+	+	+	+/-	+
III-6c	+	+	+/-	+	+	+/-	+/-
III-6d	+	+	+/-	+	+	+/-	+
III-6e	+	+	+	+	+/-	+	+
III-6f	+	+	+	+	+/-	+/-	+
III-6g	+	+	+	+	+	+/-	+
III-6h	+	+	+	+	+	+	+
III-6i	+	+	+	+	+/-	+/-	+

^a Solubilities taken of 10-20 mg sample of polymer in 1-2 mL of solvent.

‘+’ fully soluble at room temperature, ‘+/-’ partially soluble at room temperature

III.4.2. Structural Characterization

The IR spectrum of each ketone polymer displayed C=O stretching in the range from 1652 cm⁻¹ to 1658 cm⁻¹. The data from all the ¹H NMR and ¹³C NMR spectra of poly(aryl ether ketone)s **III-6(a-d,f-h)** are recorded in the experimental section. Figure III.10 displays the aromatic region of the ¹H NMR spectrum of the BPA-containing PAEK **III-6a**. The assignment was based on COSY experiments. Evidence of the unsymmetric

nature of these polymers was observed with the presence of three singlets at 1.69 ppm in the ^1H NMR spectrum of **III-6a**. Figure III.10 also shows how the aromatic protons of the BPA unit experience different magnetic environments because they do not appear as a simple doublet of doublets as would be expected from any AB splitting system.

III.4.3. Thermal and Mechanical Properties

III.4.3a. Glass Transition Temperatures

Glass transition temperatures (T_g) were determined by differential scanning calorimetry (DSC). The T_g of poly(aryl ether ketone)s **III-6(a-i)** are reported in Table III.8 and compared to the 1,4-phenylene-derived PAEK. In each case, the insertion of 1,4-naphthylene resulted in an increase in T_g for the PAEK. The increase is most notable for the 1,4-hydroquinone derivative (**III-6f**). The symmetric equivalent is PEEK which has a T_g of 144 °C and T_m of 335 °C. Incorporation of the naphthylene ring into PEEK resulted in an increase of 44 °C ($T_g = 188$ °C) and no crystalline behaviour is detected by DSC. The smallest increase in T_g was found with **III-6d** ($T_g = 288$ °C, $\Delta T_g = 14$ °C), the polymer containing TMBP. The smaller increase is due to the already high T_g attained with four methyl groups on the bisphenol unit ($T_g = 266$ °C). Otherwise, increases ranged from 24 to 44 °C, which are quite significant. The poly(aryl ether ketone)s, as a whole, display lower glass transition temperatures than their poly(aryl ether sulfone) counterparts.

Figure III.10. The 400 MHz ^1H NMR spectrum (6.8 to 8.5 ppm) of BPA-based PAEK

III-6a

Table III.8. T_g and T_d of PAEK III-6(a-i)

PAEK			$\Delta T_g^c (^{\circ}\text{C})$	$T_d^d (^{\circ}\text{C})$
III-6a	189	155	34	497
III-6b	199	175	24	517
III-6c	210	170	40	536
III-6d	280	266	14	440
III-6f	188	144 ($T_m = 335^{\circ}\text{C}$)	44	506
III-6g	272	252	20	519
III-6h	253	214	39	481
III-6i	290	253 ^{15a}	37	482

^aGlass transition temperature ($^{\circ}\text{C}$) of unsymmetric naphthylene-containing polyketone^bGlass transition temperature ($^{\circ}\text{C}$) of symmetric phenylene-containing polyketone²^cThe increase in T_g of unsymmetric polyketone over symmetric polyketone^dThe decomposition temperature at 5% weight loss.

III.4.3b. Decomposition Temperatures

The decomposition temperatures (T_d), as assessed by the onset temperature of 5% weight loss by TG, occurred in the range of 440–536 $^{\circ}\text{C}$ in nitrogen for polyketones III-6(a-i) (Table III.8). The polymer which again displayed the lowest T_d by more than 40 $^{\circ}\text{C}$ is III-6d ($T_d = 440^{\circ}\text{C}$). The presence of TMBP is believed to impart thermal instability due to the presence of four methyl groups in the repeat structure. The poly(aryl ether ketone)s, as a whole, display higher decomposition temperatures than their poly(aryl ether sulfone) counterparts.

III.4.3c. Young's Moduli

Thin rectangular strips of polymer films cast from chloroform solution were used to measure Young's modulus in the tensile stress-strain mode. The moduli varied from 0.42- 2.59 GPa for the unsymmetric polyketone series (Table III.9). The Young's modulus of PEEK was measured using the same procedure and gave a E' of 1.9 GPa. When compared to **III-6f**, its unsymmetric equivalent, it appeared that 1,4-naphthylene insertion increased the tensile strength for this particular polyketone.

Table III.9. Young's Moduli of Various Unsymmetric PAEK

PAEK	III-6a	III-6b	III-6c	III-6d	III-6f	III-6g	III-6h
Bisphenol	BPA	6F-BPA	BP	TMBP	HQ	HBP	PP
E' (GPa)	1.99	2.59	0.42	0.76	2.39	3.25	2.37

III.4.3. Gas Transport Properties

Tough dense films were cast from chloroform solution of the BPA and TMBP-based 1,4-naphthylene-containing PAEK (**III-6a** and **III-6d**) in order to study their gas transport properties and results are reported in Table III.10. For comparison, results of the 6F-BPA and HFP-based 1,4-naphthylene-containing PAEK (**III-6b** and **III-6g**)¹⁶, PEEK¹⁷ and symmetrical TMBP-containing poly(aryl ether ketone)¹⁸ and related symmetrical BPA and 6F-BPA-based PAEK¹⁹ are shown.

As mentioned in chapter one, poly(aryl ether ketone)s generally have poor gas transport properties as indicated by PEEK's unusually low permeabilities,¹⁷ i.e. $P(O_2) = 0.26$ Barrer, $P(CO_2) = 0.96$ Barrer. Therefore, PAEK have not been studied as much and the literature does not contain as much gas transport data for direct comparison as with the polysulfones.

Direct comparison of the TMBP-based 1,4-naphthylene PAEK (**III-6d**) to its 1,4-phenylene derivative¹⁸ was possible and showed that while the selectivities increased marginally (i.e. $\alpha(O_2/N_2)$ from 4.9 to 5.0 and $\alpha(CO_2/CH_4)$ from 19 to 24), a slight decrease is observed with the permeabilities (Table III.10). And so while the TMBP-based polyketone series exhibit the highest permeabilities of the PAEK, 1,4-naphthylene insertion does not impose significant changes in the gas transport properties.

A direct comparison of the BPA-based 1,4-naphthylene PAEK **III-6a** was not possible, but a closely related 1,4-phenylene-based PAEK containing the BPA moiety in its repeat unit (Figure III.11) exists¹⁹ and gas transport data is reported in Table III.10. A significant increase in selectivity towards CO₂ and CH₄ is noted, i.e. α (CO₂/CH₄) of 59 for **III-3a** which contains the 1,4-naphthylene unit over that of the 1,4-phenylene derivative (α (CO₂/CH₄) = 20). Likewise, the selectivity of the oxygen/nitrogen pair also increases from 5.7 to 8.0. The permeabilities remained approximately the same (Table III.10).

Figure. 11. Structures of BPA and TMBP-based PAEK

The gas transport properties of the 6F-BPA and HPF-based 1,4-naphthylene poly(aryl ether ketone)s (**III-6b** and **III-6g**) were measured by Moulinie¹⁶. Again, direct comparisons were not possible, but data for a 6F-BPA-related PAEK exists¹⁹ (Figure III.12) and all are shown in Table III.10. Insertion of 1,4-naphthylene in the 6F-BPA PAEK improved selectivities yet decreased permeabilities. In comparing **III-6b** to **III-6a**,

increases in permeabilities are noted; they are attributed to the larger free volume introduced by the presence of larger fluorine atoms of 6F-BPA than the hydrogen atoms of BPA. Again, these increases come at the cost of lower selectivities. There are no data for direct comparison of the HFP-based 1,4-naphthylene PAEK (**III-6g**). Yet, it is interesting to note that the use of the bulky bisphenol, 9,9-bis(4-hydroxyphenyl)fluorene, improved permeabilities only slight higher than BPA (**III-6a**) and not as high as 6F-BPA (**III-6b**).

In summary, when comparisons were possible, it was found that 1,4-naphthylene insertion into the PAEK series served to effect increases in permselectivities at the cost of lowering permeabilities. The same trend was noted for the PAES series. In some cases, the decrease in permeability is small. In both series, the BPA-based poly(aryl ether) was most sensitive to increases in selectivity resulting in α (CO_2/CH_4) as high as 59. Thus the possibility of using 1,4-naphthylene insertion in other PAEK and PAES as a strategy to improve selectivities with minimal losses in permeabilities seems plausible.

Figure III.12. Structures of 6F-BPA and HFP-based PAEK

Table III.10. Gas Properties of 1,4-Phenylene and 1,4-Naphthylene-Based PAEK

	^a P(O ₂) Barrer	P(N ₂) Barrer	α^b (O ₂ /N ₂)	P(CO ₂) Barrer	P(CH ₄) Barrer	α (CO ₂ /CH ₄)
PEEK ¹⁷	0.26	0.04	6.5	0.96	0.03	31
III-6a ¹⁴	1.20	0.15	8.0	4.70	0.08	59
BPA ¹⁹	1.1	0.21	5.7	4.6	0.23	20
III-6d ¹⁴	4.20	0.84	5.0	19.0	0.79	24
TMBP ¹⁸	4.76	0.97	4.9	19.4	1.02	19
III-6b ¹⁶	1.85	0.32	5.7	6.04	0.21	29
6FBPA ¹⁹	3.7	0.76	4.8	12.9	0.54	24
III-6g ¹⁶	1.42	0.22	6.4	4.97	0.19	26

^a P is the gas permeability with the specified gas, taken at 150 psi.

^b α is the gas permselectivity towards the specified gas pair.

III.5. Conclusions

Four new dihalo ketone activated monomers, **III-1(a-d)**, were successfully designed and synthesized. These monomers, on the most part, formed high molecular polymers with various commercially available bisphenols. BPA proved to be the most discriminating of the bisphenols when paired with monomers containing the chlorobenzoyl moiety, **III-1c** and **III-1d**, to form low molecular weight polymers.

The predicted facile displacement of chlorine from the naphthyl moiety in polycondensation with bisphenols relative to the phenyl ring has been demonstrated. Copolymerization to form high molecular weight polymers was possible with a ratio as low as 1 to 4 of the dichloro to difluoro monomers (**III-1d** to **III-1a**). Model studies showed that while the suspected *in-situ* halogen exchange occurs, it is not likely to play a significant role in the actual polymerization mechanism due to its slow rate.

The successful polymerization of the unsymmetric ketone monomer **III-1b** with various bisphenols permitted the incorporation of 1,4-naphthylene into a new series of poly(aryl ether ketone)s. In all cases, the insertion of the naphthylene ring into PEEK-like polymers resulted in increases in T_g . T_d values ranged from 440°C to 536 °C. 1,4-Naphthylene insertion resulted in polymers with improved permeabilities over the 1,4-phenylene equivalent counterparts.

The insertion of 1,4-naphthylene into the PAEK series served to effect increases in permselectivities at the cost of lowering permeabilities. Since the same trend was noted in the PAES series, the possibility of using 1,4-naphthylene insertion in other PAEK and

PAES as a strategy to improve selectivities with minimal losses in permeabilities is introduced.

III.6. Experimental Section

Materials

Reagent grade tetramethylene sulfone (TMSO_2) was fractionally distilled under vacuum ($120^\circ\text{C}/3\text{ mmHg}$). Anhydrous potassium carbonate was ground in a crucible before use. The bisphenols were purified as reported in chapter two. N-Methyl-2-pyrrolidinone (NMP), N,N-dimethylacetamide (DMAc) and all other reagents were purchased from Aldrich Chemical Co. and used directly.

Measurements

The monomers and polymers were characterized using techniques as detailed in chapter two.

Monomer Syntheses

1-Chloro and 1-fluoronaphthalenes readily undergo the Friedel-Crafts reaction with the corresponding 4-halobenzoylchlorides to form the four monomers **III-1(a-d)**. The following is a typical procedure for the synthesis of these monomers.

To a 100 mL, three-necked, round-bottomed flask containing a magnetic stirring bar flame dried under nitrogen flow were added 4-fluorobenzoyl chloride (5.060 g, 31.83 mmol), 1-fluoronaphthalene (5.120, g, 31.83 mmol) and dry CH_2Cl_2 (30mL). The reaction flask was then cooled in an ice bath (5°C) before anhydrous AlCl_3 (35.10g, 38.50 mmol) was added slowly. The solution turned yellow then a dark red/brown color. After an hour the solution was quenched with iced water and turned yellow. The organic layer

was washed with aqueous HCl (5%), aqueous NaOH (5%), brine (23%) and water. The organic layers were combined and dried over anhydrous MgSO_4 . The solvent was removed under reduced pressure to give 4,4'-difluorobenzo-1'-naphthone (**III-1a**) as white crystals and recrystallized from hexane. Yield: 71%; m.p. 84-86 °C; IR (KBr, cm^{-1}) 1657 (C=O), 1230 (C-O); MS (EI, m/e, relative intensity %) 173 (M^+ - PhF, 100), 268 (M^+ , 87.6), 123 (COPhF^+ , 68.9), 145 (M^+ - COPhF, 63.3), 95 (PhF^+ , 54.4); ^1H NMR (400 MHz, CDCl_3): δ 8.19 (m, 1H), 8.15 (m, 1H), 7.88 (dd, 2H, $J_{\text{H-F}} = 5.6$ Hz, $J_{\text{H-H}} = 8.8$ Hz), 7.60 (m, 2H), 7.46 (dd, 2H, $J_{\text{H-F}} = 5.2$ Hz, $J_{\text{H-H}} = 8.0$ Hz), 7.17 (dd, 1H, $J_{\text{H-F}} = 10.0$ Hz, $J_{\text{H-H}} = 8.0$ Hz), 7.14 (t, 2H, $J_{\text{H-H}} = 8.8$ Hz, $J_{\text{H-F}} = 8.8$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 195.3, 165.9 ($^1J_{\text{C-F}} = 250$ Hz), 160.5 ($^1J_{\text{C-F}} = 260$ Hz), 134.8, 133.0 ($^3J = 10$ Hz), 132.8, 132.1, 128.8 ($^3J = 10$ Hz), 128.4, 126.9, 125.7, 124.1, 121.0, 115.7 ($^2J = 20$ Hz), 108.2 ($^2J = 30$ Hz); ^{19}F NMR (300 MHz, DMSO-d_6): δ -104.9 (Ph-F), -117.2 (Naph-F).

4'-Chloro-4-fluorobenzo-1'-naphthone (**III-1b**): white cubic crystals, yield (hexane/cyclohexane) 63%; m.p. 117-118 °C; IR (KBr, cm^{-1}) 1656 (C=O), 1228 (C-O); MS (EI, m/e, relative intensity %) 123 (COPhF^+ , 100), 284 (M^+ , 92.0), 189 (M^+ - PhF, 76.3), 95 (PhF^+ , 66.6), 161 (M^+ - COPhF, 41.7); ^1H NMR (400 MHz, CDCl_3): δ 8.39 (d, 1H, $J_{\text{H-H}} = 8.8$ Hz), 8.05 (d, 1H, $J_{\text{H-H}} = 8.4$ Hz), 7.88 (d of d, 2H, $J_{\text{H-H}} = 8.8$ Hz, $J_{\text{H-F}} = 5.6$

Hz), 7.66 (m, 1H), 7.63 (d, 1H, $J_{\text{H-H}} = 7.6$ Hz), 7.57 (m, 1H), 7.47 (d, 1H, $J_{\text{H-H}} = 7.6$ Hz), 7.13 (t, 2H, $J_{\text{H-H}} = 8.8$ Hz, $J_{\text{H-F}} = 8.8$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 196.1, 166.6 ($^1J_{\text{C-F}} = 250$ Hz), 135.9, 135.8, 134.9, 133.6 ($^3J_{\text{C-F}} = 10$ Hz), 132.5, 131.6, 128.6, 128.3, 127.8, 126.6, 125.5, 125.4, 116.4 ($^2J_{\text{C-F}} = 20$ Hz); ^{19}F NMR (300 MHz, DMSO-d_6): δ -104.3.

4-Chloro-4'-fluorobenzo-1'-naphthone (**III-1c**): white fluffy needles, yield (EtOH) 63%; m.p. 84 °C; IR (KBr, cm^{-1}) 1645 (C=O), 1247 (C-O); MS (EI, m/e, relative intensity %) 173 ($\text{M}^+ - \text{PhCl}$, 100), 284 (M^+ , 55.7), 145 ($\text{M}^+ - \text{COPhCl}$, 55.3), 249 ($\text{M}^+ - \text{Cl}$, 31.9), 139 (COPhCl, 36.9); ^1H NMR (400 MHz, CDCl_3): δ 8.19 (m, 2H), 7.79 (d, 2H, $J_{\text{H-H}} = 8.4$ Hz), 7.61 (m, 2H), 7.55 (dd, 1H, $J_{\text{H-H}} = 8.0$ Hz, $J_{\text{H-F}} = 5.6$ Hz), 7.45 (d, 2H, $J_{\text{H-H}} = 8.4$ Hz), 7.17 (dd, 1H, $J_{\text{H-H}} = 8.0$ Hz, $J_{\text{H-F}} = 10.0$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 195.6, 160.7 ($^1J_{\text{C-F}} = 250$ Hz), 139.7, 136.8, 132.9, 131.9, 131.7, 129.1 ($^2J_{\text{C-F}} = 10$ Hz), 128.8, 128.5, 127.0, 125.7, 124.0, 121.0, 108.2 ($^3J_{\text{C-F}} = 30$ Hz); ^{19}F NMR (300 MHz, DMSO-d_6): δ -116.8.

4,4'-dichlorobenzo-1'-naphthone (**III-1d**): white prismatic needles, initially recrystallized in cyclohexane to remove orange impurities (45% crude yield) then washed in MeOH and finally recrystallized in EtOH, final yield 14%; m.p. 132 °C; IR (KBr, cm^{-1}) 1645 (C=O), 1248 (C-O); MS (EI, m/e, relative intensity %) 189 (M^+ - PhCl, 100), 139 (COPhCl, 73.2), 300 (M^+ , 67.7), 265 (M^+ - Cl, 54.3), 161 (M^+ - COPhCl, 52.0); ^1H NMR (400 MHz, CDCl_3): δ 8.39 (d, 1H, $J_{\text{H-H}} = 8.0$ Hz), 8.07 (d, 1H, $J_{\text{H-H}} = 8.0$ Hz), 7.79 (d, 2H, $J_{\text{H-H}} = 8.8$ Hz), 7.67 (ddd, 1H, $J_{\text{H-H}} = 8.0$ Hz, $J_{\text{H-H}} = 7.6$ Hz, $J_{\text{H-H}} = 1.2$ Hz), 7.63 (d, 1H, $J_{\text{H-H}} = 7.6$ Hz), 7.60 (ddd, 1H, $J_{\text{H-H}} = 8.0$ Hz, $J_{\text{H-H}} = 7.6$ Hz, $J_{\text{H-H}} = 1.2$ Hz), 7.49 (d, 1H, $J_{\text{H-H}} = 7.6$ Hz), 7.47 (d, 2H, $J_{\text{H-H}} = 8.8$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 195.9, 139.7, 135.9, 135.2, 134.7, 131.6, 131.4, 130.7, 128.6, 127.8, 127.4, 127.1, 125.6, 124.6, 124.5.

Polymerizations

General procedures for both solvent systems are described below.

NMP/Toluene. A 50 mL, three necked round bottom flask equipped with a Dean Stark trap connected with condenser and a nitrogen purge line was flame dried. **III-1a** (1.07g, 4.000 mmol), BPA (0.91g, 4.000 mmol) and K_2CO_3 (1.11 g, 8.000 mmol) were added to the flask with NMP (10mL) and toluene (20mL). The mixture was purged with nitrogen and stirred for 20 mins, then heated slowly to 120-130 °C. The water and toluene were co-distilled while deoxygenated toluene was introduced. The solution turned yellow initially then darker orange. After 2-3 h, the temperature was increased to 180 °C for polymerization to occur. The solution turned green and became viscous after

one hour at higher temperature. The reaction was monitored by GPC and stopped after 2 h. After letting it cool, it was diluted with NMP (9 mL), then dropped into methanol containing a few drops of concentrated HCl. All the polymers were purified by dissolving in chloroform, filtering through Celite to remove any salts and precipitating into methanol again. The low molecular weight fractions were removed in all cases by reverse precipitation. This technique involved adding methanol dropwise into a chloroform solution of the polymer. This coagulated to form a gummy residue and a white cloudy solution consisting of the lower molecular weight fractions. The cloudy solution was then decanted and the gummy residue was dissolved in chloroform (5-10 mL) and precipitated finally into methanol (150 mL).

TMSO₂/Chlorobenzene. A 50 mL, three-necked, round-bottomed flask equipped with a Dean-Stark trap connected with a condenser and a nitrogen purge line was flame dried. A mixture of dihalide monomer (3.000 mmol), bisphenol (3.000 mmol), potassium carbonate (0.749 g, 5.400 mmol), TMSO₂ (4 mL) and chlorobenzene (4 mL) were heated to 210 °C in an oil bath in 30-40 min. Water formed during the reaction was removed as an azeotrope with chlorobenzene. The oil bath temperature was maintained at 210 °C for 2-4 h depending on the progress of the polymerization. The reaction was monitored by GPC and stopped when the molecular weight was seen to decrease after an initial decrease. The polymer was then precipitated into methanol containing a few drops of concentrated acid and collected by filtration. All polymers were purified by dissolving in chloroform (~100 mL), filtering through Celite to remove any salts and precipitating into

methanol. Reverse precipitation, as described in the above procedure, was performed in cases except polymer **III-6e**.

Polymer **III-6a**: Yield 96%; IR (film, cm^{-1}) 1652 (C=O), 1240 (C-O); UV/VIS (CHCl_3) λ 296.11 nm; ^1H NMR(400 MHz, CDCl_3): δ 8.37 (m, 1H), 8.19 (m, 1H), 7.81 (d, 2H, $J_{\text{H-H}} = 8.4$ Hz), 8.53 (m, 2H), 7.46 (d, 1H, $J_{\text{H-H}} = 8.0$ Hz), 7.24 (m, 4H), 7.03 (m, 2H), 6.96 (m, 4H), 6.80 (m, 1H), 1.69 (3s, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 195.93, 162.08, 156.39, 154.24, 153.28, 146.92, 146.84, 146.58, 146.49, 133.12, 132.78, 132.65, 130.91, 128.96, 128.33, 128.00, 126.56, 126.36, 125.84, 122.33, 119.67, 119.37, 117.06, 109.49, 42.35, 31.01.

Polymer **III-6b**: Yield 89%; IR (film, cm^{-1}) 1658 (C=O), 1244 (C-O); UV/VIS (CHCl_3) λ 290.00 nm; ^1H NMR (400 MHz, CDCl_3): δ 8.30 (m, 1H), 8.20 (m, 1H), 7.58 (m, 2H), 7.54 (d, 1H, $J_{\text{H-H}} = 7.6$ Hz), 7.41(m, 4H), 7.10(m, 4H), 7.06 (d, 2H, $J_{\text{H-H}} = 8.6$ Hz), 6.97 (d, 1H, $J_{\text{H-H}} = 7.9$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 195.97, 160.80, 157.52, 156.40, 154.91, 133.86, 132.80, 132.01, 128.95, 128.66, 127.48, 128.25, 126.91, 126.81, 125.94, 122.25, 119.08, 118.52, 118.17, 111.50.

Polymer **III-6c**: Yield 93%; IR (film, cm^{-1}) 1654 (C=O), 1237 (C-O); UV/VIS (CHCl_3) λ 288.47 nm; ^1H NMR (400 MHz, CDCl_3): δ 8.40 (m, 1H), 8.22 (m, 1H), 7.88 (d, 2H, $J_{\text{H-H}} = 8.6$ Hz), 7.58 (m, 6H), 7.52 (d, 1H, $J_{\text{H-H}} = 7.9$ Hz), 7.21 (d, 2H, $J_{\text{H-H}} = 7.7$ Hz), 7.14 (d, 2H, $J_{\text{H-H}} = 7.00$ Hz), 7.04 (d, 2H, $J_{\text{H-H}} = 8.4$ Hz), 6.90 (d, 1H, $J_{\text{H-H}} = 7.9$ Hz); ^{13}C NMR (100

MHz, CDCl₃) δ 195.90, 161.89, 156.11, 154.08, 154.04, 136.86, 136.75, 136.46, 136.35, 133.30, 132.84, 132.74, 131.28, 128.88, 128.53, 128.11, 126.68, 126.53, 125.89, 122.35, 120.49, 120.02, 117.29, 110.11.

Polymer **III-6d**: Yield 92%; IR (film, cm⁻¹) 1652 (C=O), 1228 (C-O); UV/VIS (CHCl₃) λ 285.42 nm; ¹H NMR (400 MHz, CDCl₃): δ 8.65 (m, 1H) 8.31 (m, 1H), 7.86 (m, 2H, J_{H-H} = 8.7 Hz), 7.64 (m, 2H), 7.46 (m, 1H), 7.38 (4s, 4H), 6.88 (m, 2H), 6.44 (m, 1H), 2.23 (4s, 12H); ¹³C NMR (100 MHz, CDCl₃) δ : 195.98, 161.72, 155.75, 150.45, 150.08, 137.98, 137.93, 132.96, 132.58, 131.41, 129.74, 129.57, 128.08, 127.83, 126.18, 125.95, 125.23, 124.35, 122.27, 114.43, 104.47, 16.55, 16.47, 16.35, 16.25.

Polymer **III-6f**: Yield 95%; IR (film, cm⁻¹) 1653 (C=O), 1229 (C-O); UV/VIS (CHCl₃) λ 297.31 nm; ¹H NMR(400 MHz, CDCl₃): δ 8.40 (m, 1H), 8.21 (m, 1H), 7.86 (d, 2H, J_{H-H} = 8.8 Hz), 7.57 (m, 1H), 7.50 (m, 1H), 7.16 (d, 2H, J_{H-H} = 13.8 Hz), 7.12 (d, 2H, J_{H-H} = 13.8 Hz), 7.00 (m, 2H), 6.83(m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 195.85, 162.18, 162.04, 156.32, 153.02, 152.72, 152.01, 151.71, 133.26, 132.83, 132.76, 131.14, 128.88, 128.83, 128.16, 126.56, 126.47, 125.90, 122.26, 121.87, 121.79, 121.51, 121.41, 116.99, 116.92, 109.44, 109.32.

Polymer **III-6g**: Yield 89%; IR (film, cm⁻¹)1654 (C=O), 1239 (C-O); UV/VIS (CHCl₃) λ 308.33 nm, 297.64 nm, 276.25 nm; ¹H NMR (400 MHz, CDCl₃): δ 8.33 (m, 1H), 8.17 (m, 1H), 7.77(m, 4H), 7.52 (m, 2H), 7.40 (m, 7H), 7.24(m, 4H), 6.94 (m, 6H), 6.77 (d,

^1H , $J_{\text{H-H}} = 7.5 \text{ Hz}$); ^{13}C NMR (100 MHz, CDCl_3): δ 195.86, 161.74, 156.01, 155.54, 154.24, 150.98, 142.05, 141.54, 140.02, 133.17, 132.72, 132.63, 131.00, 129.68, 128.89, 128.02, 127.87, 127.73, 126.54, 126.41, 126.03, 125.80, 122.25, 120.35, 119.77, 119.42, 117.20, 109.80.

Polymer **III-6h**: Yield 91 %; IR (film, cm^{-1}) 1772 (C=O, lactam), 1654 (C=O, conjugated), 1240 (C-O); UV/VIS (CHCl_3) λ 286.94 nm; ^1H NMR (400 MHz, CDCl_3): δ 8.28 (m, 1H), 8.17 (m, 1H), 7.95 (d, 1H, $J_{\text{H-H}} = 7.8 \text{ Hz}$), 7.82 (d, 2H, $J_{\text{H-H}} = 8.7 \text{ Hz}$), 7.71 (t, 1H), 7.54 (m, 4H), 7.47 (d, 1H, $J_{\text{H-H}} = 7.9 \text{ Hz}$), 7.36 (m, 4H), 7.05 (m, 4H), 6.98 (d, 2H, $J_{\text{H-H}} = 8.6 \text{ Hz}$), 6.86 (d, 1H, $J_{\text{H-H}} = 7.9 \text{ Hz}$); ^{13}C NMR (100 MHz, CDCl_3): δ 195.77, 169.45, 169.41, 161.37, 161.28, 157.13, 155.96, 155.38, 151.90, 151.84, 151.77, 136.88, 136.80, 136.39, 136.30, 134.37, 133.58, 132.81, 132.72, 131.71, 129.64, 129.01, 128.67, 128.16, 126.75, 126.67, 126.25, 125.90, 125.56, 124.01, 122.24, 119.78, 119.20, 117.69, 110.86, 91.02, 90.95, 90.88.

Polymer **III-6i**: Made by Jeff Franklin. Yield 85%; IR (film, cm^{-1}) 1670 (C=O), 1240 (C-O); UV/VIS (CHCl_3) λ : 308.33 nm.

Copolymerization

Four copolymerizations were done in varying molar ratios of difluoro (**III-1a**) to dichloro (**II-1b**) monomer (i.e. 1:1, 1:2, 1:4 and 1:9) with BPA on a 3 mmol scale. A typical procedure for the copolymerization is as follows: A 50 mL, three-necked, round-

bottomed flask equipped with a Dean-Stark trap connected with a condenser and nitrogen purge line was flame dried. A mixture of **III-1a** (0.402 g, 1.500 mmol), **III-1d** (0.450 g, 1.5 mmol), K_2CO_3 (0.746 g, 5.400 mmol), bisphenol A (0.685 g, 3.000 mmol), $TMSO_2$ (4mL) and chlorobenzene (4 mL) were heated to 210°C in an oil bath in 40 min. Water formed during the reaction was removed as an azeotrope with chlorobenzene. The oil bath temperature was maintained at 210 °C for 2 h. $TMSO_2$ (2 mL) was added to the system when stirring became difficult. The progress of the polymerization was followed by GPC and the reaction was stopped when the molecular weight was seen to decrease after an initial increase. The reaction mixture was then poured into methanol to precipitate the polymer which was collected by filtration, redissolved in solvent and filtered through Celite to remove any salts and precipitated into methanol. In cases of molecular weights greater than 30,000, oligomers were removed by reverse precipitation.

Model Reaction 1

A 50 mL, three-necked, round bottomed flask was set up with a Dean-Stark trap, condenser and nitrogen purge line as before. **III-1d** (0.990 g, 3.000 mmol), K_2CO_3 (0.749 g, 5.400 mmol), $TMSO_2$ (4 mL) and chlorobenzene (3 mL) were added to the system. The reaction mixture was then heated to 210 °C in 40 min and stirred. Standards of the four possible halogen exchange products (**III-1a**, **III-1b**, **III-1c** and **III-1d**) had been made

previously. The progress of the reaction was monitored by HPLC and retention times were used to identify peaks. Relative abundances were determined using the peak area of the four monomers. This did not include the area of the unidentified compound at a lower retention time which emerged during the course of the reaction, small at first, larger at the end. This was believed to be either a decomposition product of TMSO_2 or a reductive dehalogenation product.

Model Reaction 2

A 50 mL, three-necked, round bottomed flask with Dean-Stark trap, condenser and nitrogen purge line was flame dried as before. **III-1a** (0.429 g, 1.500 mmol), phenol (0.282 g, 3.00 mmol), K_2CO_3 (0.749 g, 5.400 mmol), TMSO_2 (4 mL) and chlorobenzene (3 mL) were added to the system and heated to 210 °C. After 1h of heating, **III-1d** (0.450 g, 1.500 mmol) was added. The reaction was again monitored by HPLC.

End-Capped BPA-Based PAEK

A Dean-Stark trap with a condenser and 50 mL, round-bottomed flask was set up as before and flame dried. Monomer **III-1a** (2.144 g, 8.000 mmol), BPA (1.806 g, 7.920 mmol), K₂CO₃ (2.208 g, 16.000 mmol) and 3,5-di-*tert*-butylphenol (0.055 g, 0.160 mmol), TMSO₂ (10 mL) and chlorobenzene (3 mL) were added to the reaction flask. The temperature was maintained at 170 °C for 1.5 h to azeotrope off water. Afterwards, the reaction was increased to 210 °C for 30 min. More TMSO₂ (6 mL) was added to allow stirring to continue. The reaction was stopped 30 min later and worked up as as before with reverse precipitation. $\eta_{inh} = 0.47$ dL/g. IR (film) 1653 cm⁻¹ (C=O), ¹H NMR (CHCl₃, 400 MHz) δ 8.38 (m, 1H), 8.19 (m, 1H), 7.82 (d, 2H, ³J_{H-H} = 8.5 Hz), 7.53 (m, 2H), 7.47 (d, 1H, ³J_{H-H} = 7.9 Hz), 7.25 (m, 4H), 7.03 (d, 2H, ³J_{H-H} = Hz), 6.96 (d, 4H), 6.80 (d, 1H), 1.69 (3s, 6 H), 1.30 (2s, 0.28 H).

III.7. References

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IV.1. Introduction

The ultimate goal was to incorporate an optically active chiral element into a polymer. If successful, the resulting polymers are expected to possess some unique properties inherited from these chiral components. Prior to dealing with optically active polymers, a new route to the introduction of axial and helical chiral units into poly(aryl ether)s should be explored using a racemic starting material.

IV.1.1. Axial and Helical Chirality

Ortho-substituted biphenyls and binaphthyls (Figure IV.1) are examples of *atropisomerism* or 'axial chirality' which due to restricted bond rotation about a single bond (from Greek *a* meaning not, and *tropos* meaning turn).¹ Biphenyls and binaphthyls therefore exist in two conformational stereoisomers which can often be isolated depending on the number and size of ortho substituted groups.

Figure IV.1. *Ortho*-substituted biphenyls and binaphthyls

Helicenes exist as pairs of enantiomers, denoted P and M, as seen in Figure IV.2.² The helicene is labeled 'P' when, as one progresses along the axis of the helix away from the observer, the sense of twist is clockwise.¹ Likewise, it is denoted 'M' when the corresponding sense of twist is counter-clockwise. Helicenes are characterized by very large optical rotations in the order of 3000°.

Figure IV.2. Right and left handed [6]helicenes

IV.1.2. 1,1'-Binaphthalene and Helicene-Based Polymers

A widely used starting material for functionalized chiral binaphthyls is 1,1'-binaphthyl-2,2'-ol. It can be resolved in large quantities³ and has been functionalized to yield a variety of monomers such as dibromides for chiral poly(arylene)s,^{4,5} a diamine and diacid chloride for polyamides⁶ and a dianhydride for aromatic polyimides.⁷

Figure IV.3. 1,1'-Binaphth-2,2'-ol-based polymers (a) polyarylenes,^{4b} (b) polyamides⁶ and (c) polyimides⁷

In contrast to chiral binaphthyl systems, helicene-based chiral polymers have received less attention, partially due to difficulties in the synthesis and functionalization of helicenes. Generally, helicenes are made in a multi-step sequence which usually involves a

photochemical cyclization of stilbene-type compounds and are difficult to functionalize with polymerizable groups.² To date, only a few helicene-based polymers have been synthesized, such as an optically active metallocene polymer derived from a functionalized [6]helicene,⁸ the polyimides derived from a [5]helicene dianhydride synthesized by Frimer et al. and several [5]helicene AB-type amino anhydride and AA-type diamines reported by Wang's group.⁹

Figure IV.4. [5]Helicene-based polyimides by (a) Frimer^{9b} and (b) Wang^{9c,d}

Wang and co-workers have also demonstrated the introduction of the [5]helicene unit into polyimides via chemical transformation of tetrahydro[5]helicene-based precursor polymers.^{9d}

IV.1.3. Precursor Strategy

The following precursor strategy was attempted in order to incorporate the helicene moiety into poly(aryl ether)s. The transformation of the 2,2'-dibenzoylbiphenyl

unit into a phenanthrene moiety in the backbone of poly(arylene ether)s via a de-oxy-olefination reaction using Lawesson's reagent (A to A', Scheme IV.1) was previously reported by Wang and Zhang.¹⁰ By analogy, the 2,2'-dibenzoyl-1,1'-binaphthyl unit in a polymer should undergo the same de-oxy-olefination reaction, yielding the chiral [5]helicene unit (B to B', Scheme IV.1). Thus, this polymer transformation would allow the introduction of helical chiral units into a polymer via a chirality transformation of a precursor polymer containing axial units.

Scheme IV.1. Intramolecular de-oxy-olefination of dibenzoylbiaryls

IV.1.4. Rationale and Objectives

The introduction of the axial chiral element into the polymer main chain is made possible by the design and synthesis of a novel monomer, 2,2'-bis(4-fluorobenzoyl)-1,1'-binaphthalene (IV-6, Figure IV.5).

Figure IV.5. 2,2'-Bis(4-fluorobenzoyl)-1,1'-binaphthalene

The two benzoyl groups are larger than the 2,2'-dihydroxy groups of the known chiral binaphthyl, 2,2'-dihydroxy-1,1'-binaphthalene shown in Figure IV.1. In fact, it was hoped that enantiomerically pure monomer would be more stable to racemization over its 2,2'-dihydroxy counterpart.^{3,4} The fluoro groups are activated towards nucleophilic displacement in a 1:1 ketone/halide ratio which favours increased reactivity over 4,4'-difluorobenzophenone with a 1:2 ketone/halide ratio. That is, the fluorine atoms in the diketone monomer are each activated by one fluorine atom whereas in the monoketone monomer, both fluorine atoms share activation with the central carbonyl unit.

Thus, monomer IV-6 should be polymerized with a bisphenol (e.g. BPA) to make a poly(aryl ether ketone). A model reaction will be carried out in order to test the polymerizability of monomer IV-6. To demonstrate the synthetic feasibility and concept of chirality transfer, the binaphthalene-based polymer will be subjected to an intramolecular de-oxy-olefination reaction to form a [5]helicene-containing poly(arylene ether). Model reactions should be performed as well to test the efficiency of the transformation reaction.

Chiral chromatography can be used to resolve the binaphthyl monomer in order to obtain optically active starting material for polymerization. Transformation of the optically active chiral binaphthyl polymer to incorporate a [5]helicene moiety in the repeat unit could then be realized. The polymerization and transformation would fulfill the goal of incorporating an optically active chiral element into a polymer.

IV.2. Monomer Synthesis

IV.2.1. Synthesis

The monomer, 2,2'-bis(4-fluorobenzoyl)-1,1'-binaphthalene (**IV-6**), was made in six steps from commercially available 1-bromo-2-methylnaphthalene with an overall yield of 31 % (Scheme IV.2).¹¹ The known procedures¹² for the first three steps were slightly modified to accommodate the larger scale needed and the intermediates have been characterized by NMR, IR and MS.

Initially, a five-step route was investigated which, after bromination of the starting material,^{12a} involved the direct oxidation of 1-bromo-2-bromomethylnaphthalene (**IV-1**) to give 1-bromo-2-naphthaldehyde (**IV-3**) by the Sommelet reaction (Path A, Scheme IV.2).^{12a,13} But the reported yield of 60% for the Sommelet reaction could not be reproduced on a large scale. After several attempts, only 30% yield was achieved. Thus an additional step was added, namely, the hydrolysis of **IV-1** to its primary alcohol **IV-2** (Path B Scheme IV.2),^{12b} which was then oxidized to the aldehyde **IV-3** in 52% yield from the starting material.^{12c}

The aldehyde **IV-3** was then added to a solution of 4-fluorophenylmagnesium bromide to give the alcohol **IV-4**, which was oxidized using Corey's procedure^{12c} with pyridinium chlorochromate, 1-bromo-2-(4-fluorobenzoyl)naphthalene **IV-4**, was then coupled using a Ni(0) catalyst to afford the desired monomer (**IV-6**).¹⁴

Monomer **IV-6** was insoluble in most organic solvents and but could be recrystallized from 1,2-dichlorobenzene. It had a melting point of 298°C and sublimed easily to give white crystals useful for single crystal X-ray diffraction analysis.

Scheme IV.2. Synthesis of 2,2'-bis(4-fluorobenzoyl)-1,1'-binaphthalene IV-6

IV.2.2. Characterization

Comprehensive ¹H and ¹³C NMR data for compounds IV-1, IV-2 and IV-3, which were not included in original reports,¹² confirmed their structures in conjunction with MS, m.p. and IR data. Similarly, the structures of IV-4, IV-5 and IV-6 have been verified with MS, IR and NMR.

In particular, IR showed a shift in the C=O peak from 1682 cm⁻¹ in the aldehyde IV-3 to 1672 cm⁻¹ for the ketone IV-5, then finally a shift to 1657 cm⁻¹ for the monomer IV-6. MS confirmed the successful coupling of IV-5 to form IV-6 with a molecular ion peak at 498 *m/e*. Results from elemental analysis were consistent with the molecular formula of IV-6.

The ^1H NMR spectrum of **IV-6** is shown in Figure IV.6. Assignment was made for the ^1H NMR spectrum in conjunction with COSY experiment. The proton ortho to the fluorine position in the fluorobenzoyl unit (Ha) displays its characteristic triplet at 6.80 ppm ($^3J_{\text{H-H}} = 8.4$ Hz, $^3J_{\text{H-F}} = 8.4$ Hz) as was found in previous ketone monomers. The proton meta to the fluorine atom (Hb) could not be distinguished due to overlapping with protons Hg and Hd. A clear doublet was seen for Hc which couples with Hd ($^3J_{\text{H-H}} = 8.3$ Hz). The symmetry of the monomer is evident by ^1H NMR.

The ^{19}F NMR spectrum showed a single peak at -106.3 ppm which indicates a marginal increase in reactivity relative to the proven reactive monomer, 4,4'-difluorobenzophenone (-106.1 ppm). A slight increase in reactivity is expected due to the favorable 1:1 fluorine/ketone ratio in **IV-6** as opposed to the 1:2 keto/halogen ratio in 4,4'-difluorobenzophenone.

In addition to spectroscopic evidence, X-ray diffraction analysis corroborated the structure (Figure IV.7). The oxygen atoms (black) of the carbonyl groups are facing away from each other. The fluorobenzoyl groups lie parallel to each other with an average distance of 4 Å. The torsional angle (highlighted) along the axial bond between the two naphthalene rings is striped and is 72.9° .

Figure IV.6. The 400 MHz ^1H NMR spectrum (6.6 to 8.2 ppm) of IV-6

Figure IV.7. Molecular structure of monomer IV-6 as determined by X-ray diffraction

IV. 3. Polymer Synthesis

IV.3.1. Model Reaction

In order to probe the reactivity of monomer **IV-6**, a model reaction with 4-*tert*-butyl phenol was performed using standard nucleophilic displacement condensations to make the di(etherketone) product **IV-7** (Scheme IV.3). As expected, the ketone activated difluoro monomer was reactive enough to undergo quantitative nucleophilic displacement by the phenol to form the diether compound **IV-7**. The glassy white solid is more soluble than its difluoro precursor due to the introduction of the ether bonds and appeared as one spot on TLC.

Scheme IV.3. Model reaction to make ether model compound **IV-7**

FAB-MS was performed on **IV-7**, due to its high molecular weight, which indicated a $M^+ + 1$ peak at 759 m/e for the model product as expected by its structure. IR showed a C=O peak at 1664 cm^{-1} for the diether model compound (**IV-7**).

The ^1H NMR spectrum of the model compound **IV-7** is shown in Figure IV.8. Assignment was possible with 2D-COSY experiment. Doublets can be seen for Ha ($^3J_{\text{H-H}} = 8.9\text{ Hz}$) which couples with Hb, for Hj ($^3J_{\text{H-H}} = 8.8\text{ Hz}$) which couples with Hi, for Hh ($^3J_{\text{H-H}} = 8.3\text{ Hz}$) which couples with Hg and for both Hc and Hd which couple each other ($^3J_{\text{H-H}}$

= 8.5 Hz). The ^1H NMR spectrum also shows that the BPA/binaphthyl model compound **IV-8a** is highly symmetrical.

IV.3.2. Polymer Synthesis

Monomer **IV-6** was then polymerized with BPA and the phthalazinone monomer (Scheme IV.4). The same conditions (K_2CO_3 , TMSO_2 , chlorobenzene, 200°C) as the model reaction were used for the synthesis of **IV-8a**. But Cs_2CO_3 was used in conjunction with $\text{Mg}(\text{OH})_2$ according to the procedure by Hay when making **IV-8i**.¹⁵ IR showed a $\text{C}=\text{O}$ peak at 1664 cm^{-1} for the BPA polymer (**IV-8a**) and at 1669 cm^{-1} for the heterocyclic polymer **IV-8i**.

Scheme IV.4. Polymerization to form **IV-8a** and **IV-8i**

Figure IV.8. The 400 MHz ^1H NMR spectrum (6.4 - 8.0 ppm) of model compound IV-7

Figure IV.9. The 400 MHz ^1H NMR spectrum (6.5 to 8.0 ppm) of PAEK IV-8a

Figure IV.9 shows the ^1H NMR spectrum and assignment of **IV-8a** which resembles that of **IV-7**. Again clear doublets can be seen for Ha ($^3J_{\text{H-H}} = 8.8$ Hz), Hj ($^3J_{\text{H-H}} = 8.6$ Hz), Hc ($^3J_{\text{H-H}} = 8.7$ Hz) and Hh ($^3J_{\text{H-H}} = 8.5$ Hz) which couple their neighbouring proton. The symmetrical nature is also evident by the appearance of a singlet peak in the aliphatic region at 1.67 ppm.

Polymers **IV-8a** and **IV-8i** were soluble in most organic solvents like chloroform, TCE, CH_2Cl_2 , NMP and DMAc. It was possible to make a tough flexible film from chloroform solution for **IV-8a** but not for **IV-8i** which resulted only in a brittle film. Gel permeation chromatography indicated a high molecular weight of 10.1×10^4 for the BPA polymer **IV-8a** ($\eta_{\text{inh}} = 0.36$ dL/g) but a modest molecular weight of 2.47×10^4 for **IV-8i** ($\eta_{\text{inh}} = 0.19$ dL/g) (Table IV.1).

Table IV.1. Characterization of Binaphthalene-Based PAEK **IV-8a,i** and [5]Helicene-Based PAE **IV-11**

Polymer	Bisphenol	$M_w^a \times 10^{-4}$	$M_n^a \times 10^{-4}$	M_w^a/M_n	η_{inh} (dL/g) ^b	T_g (°C)	T_d^c (°C)
IV-8a	BPA	10.1	4.7	2.2	0.36	225 ^c	485
IV-8i	PZ	2.47	1.26	2.0	0.19	287 ^c	522
IV-11	BPA	8.2	4.1	2.0	0.25	265 ^d	459

^a Taken by GPC relative to polystyrene standards.

^b Inherent viscosity, 0.5 % chloroform solution at 25.0 °C.

^c Taken using normal mode DSC under N_2 flow, heating rate of 10 °C/min.

^d Taken using Oscillating DSC under N_2 flow, heating rate of 10 °C/min.

^e Taken at 5% weight loss under N_2 flow, heating rate of 10 °C/min.

Differential scanning calorimetry (DSC) indicates a glass transition temperature (T_g) of 225 °C for the BPA polymer (**IV-8a**) and 287 °C for the heterocyclic polymer (**IV-**

8i) (Table IV.1). When comparing the BPA/binaphthyl polymer (**IV-8a**) to its symmetric biphenyl equivalent ($T_g = 172^\circ\text{C}$),¹⁰ one observes an increase of 53°C in T_g . Likewise when comparing the heterocyclic/binaphthyl polymer (**IV-8i**) to its symmetric counterpart ($T_g = 237^\circ\text{C}$), an increase of 50°C is found. Thus the replacement of the biphenyl moiety by the binaphthyl moiety results in significant increases in T_g . When comparing the BPA/binaphthyl polymer (**IV-8a**) with the heterocyclic/binaphthyl polymer (**IV-8i**), a difference in T_g of 62°C . This is due to the increased rigidity of the heterocyclic monomer over the flexible BPA bisphenol.

The decomposition temperatures (T_d) as assessed by thermogravimetric analysis for 5% weight loss are 485°C and 522°C for the BPA polymer (**IV-8a**) and the heterocyclic polymer (**IV-8i**), respectively.

The UV/VIS absorbance spectra of the model compound **IV-7** and polymer **IV-8a** had a λ_{max} at 295 nm. The band is attributed to $\pi - \pi^*$ transitions of the naphthalene rings. Fluorescence spectrometry showed no emission upon excitation at ~ 294 nm. As well, no color was seen, by the naked eye, to be emitted under UV radiation. In addition to the absorbance λ_{max} at 295 nm, polymer **IV-8i** showed a λ_{max} at 264 nm which is attributed to the $\pi - \pi^*$ transitions of heterocyclic portion of the polymer.

IV.4. Polymer Transformation

IV.4.1. Transformation of Monomer and Model Compound

The de-oxy olefination was first attempted on the monomer **IV-6** to give the unique [5]helicene compound **IV-9** (Scheme IV.5).¹⁰ The model compound **IV-7** was also converted to form the [5]helicene-containing ether compound **IV-10** (Scheme IV.5).

Scheme IV.5. Transformation of monomer and model compound

The IR spectra of **IV-9** and **IV-10** both showed the complete disappearance of the carbonyl peak previously found at 1657 cm⁻¹ for the monomer **IV-6** and at 1664 cm⁻¹ for **IV-7**. The ¹³C NMR spectrum of **IV-10** also showed the disappearance of the carbonyl peak previously found at 195.74 ppm in the spectrum of the diketone model compound **IV-7**.

The ¹H NMR spectrum of **IV-10** is shown in Figure IV.10 with assignments. The internal proton (Hh) shifts from ~7.9 ppm in **IV-7** to ~8.4 ppm in **IV-10**, which is indicative of the helical nature. A case of magnetic non-equivalence is observed for Hb and

Hb' which appear to be locked by the rigid nature of the [5]helicene and show up as two separate doublets at 7.09 ppm and 7.14 ppm in the ^1H NMR spectrum of IV-10. In the case of IV-9, two separate multiplets show up at 7.15 ppm and 7.08 ppm for the two magnetically non-equivalent Hb and Hb'.

With the help of HETCOR and COSY experiments, the ^{13}C NMR spectrum of IV-10 also showed two magnetically non-equivalent peaks for the carbons attached to Hb and Hb' at 132.96 and 132.13 and two finely distinguishable peaks at 118.20 and 118.10 for the carbons attached to Ha. The ^{13}C NMR spectrum of IV-9 showed the carbons attached to Hb and Hb' are further split by the fluorine atom and appear at 133.06 ppm ($^3J_{\text{C-F}} = 8$ Hz) and 132.23 ppm ($^3J_{\text{C-F}} = 7$ Hz). Likewise, the carbons attached to Ha are split by fluorine at 114.83 ppm ($^2J_{\text{C-F}} = 21$ Hz), but it is difficult to see magnetic non-equivalence at this magnetic field strength.

The UV absorbance spectrum of IV-10 displayed two peaks centered at 268 nm and 315 nm. Unlike its diketone binaphthyl precursor, a chloroform solution of the [5]helicene model compound IV-10 appeared fluorescent to the naked eye and it was blue light emitting with a maximum emission at 435 nm under UV (315 nm) irradiation.

Figure IV.10. The 400 MHz ¹H NMR spectrum (6.8 to 8.5 ppm) of [5]helicene-based IV-10

Figure IV.12. The 400 MHz ¹H NMR spectrum (6.8 - 8.5 ppm) of [5]helicene-based PAEK IV-11a

IV.4.2. Polymer Transformation

The intramolecular cyclization reaction was then attempted on the poly(aryl ether ketone) **IV-8a** to make the [5]helicene-containing poly(aryl ether) **IV-11a** (Scheme IV.6).

Scheme IV.6. Transformation reaction to form [5]helicene-based PAE **IV-11a**

The carbonyl peak of **IV-8a** at 1664 cm^{-1} disappeared in the IR spectrum of **IV-11** (Figure IV.11). The ^{13}C NMR spectrum of **IV-11a** also showed the loss of the ketone peak at 195.71 ppm which was previously seen in the precursor polymer **IV-8a**.

Figure IV.11. IR Spectra of (a) binaphthalene-based PAEK **IV-8a** and (b) [5]helicene-based PAEK **IV-11a**

The ^1H NMR spectrum of [5]helicene-based polymer **IV-11a** was similar to the proton spectrum of the [5]helicene-based model compound (**IV-10**) (Figure IV.12). Assignment were made based on HETCOR and COSY experiments. Again, there was a downfield shift of the internal proton, Hh, by *ca.* 0.5 ppm and the magnetic non-equivalence of the carbons attached to protons Hb and Hb' showed as two doublets at 7.01 ppm and 7.06 ppm in the ^1H NMR spectrum. The ^{13}C NMR spectrum also showed two magnetically non-equivalent peaks for the carbons attached to the Hb and Hb' protons at 132.93 and 132.09 and two finely distinguishable peaks at 118.18 and 118.08 for the carbon attached to the Ha proton.

The [5]helicene polymer **IV-11a** remained soluble in chloroform from which a brittle film could be cast. The molecular weight did not suffer excessively during transformation to form **IV-11a** ($M_w = 8.2 \times 10^4$, $M_w/M_n = 2.0$, Table IV.1).

Oscillating DSC, which separates reversible from irreversible thermal events, was used to determine T_g because normal DSC failed to provide a clear T_g . The glass transition temperature was found to be 265 °C (Table IV.3), representing a 40°C increase in T_g over its starting diketone binaphthalene polymer. The phenanthracene-based polymer made from the equivalent biphenyl series had a T_g of 227°C, 38 °C lower than its [5]helicene counterpart.¹⁰ Thus the introduction of the rigid [5]helicene unit into the polymer backbone resulted in increases in chain rigidity compared to both the binaphthyl starting material and the equivalent phenanthracene series.

The onset temperature for 5% weight loss in nitrogen was found to be 459 °C for polymer **IV-11a**, 26°C lower than its binaphthyl starting material and 70 °C lower than the

similar phenanthracene polymer. Thus while the insertion of the [5]helicene unit increases the glass transition temperature compared to the binaphthyl and phenanthracene-based polymers, it does so at the cost of lowering the thermal stability of the polymer. It is believed that the [5]helicene moiety is subject to thermal rearrangements at higher temperatures.

As with the model compounds, UV absorbance showed two maxima at 268 and 315 nm for polymer **IV-11**. The polymer also appeared fluorescent showing an emission at 435 nm when excited at $\lambda = 315$ nm.

IV.5 Attempted Optical Resolution

IV.5.1. Strategies to Attain Optically Active Binaphthyl Compounds

The binaphthyl group has become quite popular in organic synthesis, largely due to its efficiency in transferring its chiral information in catalysis.¹⁶

In general, there are at least two common approaches to resolving racemic mixtures of enantiomers: (a) formation of diastereoisomers followed by separation based on different physical properties or (b) resolution by chiral chromatography.¹

Hall and Turner^{12a} were able to resolve 1,1'-binaphthyl-2,2'-dicarboxylic acid on a large scale by making the quinine salt and recrystallizing from ethanol. The diacid was found to be optically stable. 2,2'-Di(bromomethyl)-1,1'-binaphthyl was treated with an excess of l-ephedrine to give the quaternary ammonium salt which was separated easily due to their markedly different solubilities in ethanol.¹⁷

The pursuit of optically pure 1,1'-binaphthyls by asymmetric synthesis using chiral catalysis has enjoyed more attention in recent years. Miyano's group reported the partial asymmetric synthesis of 1,1'-binaphthyls via the Ullmann coupling reaction of chiral alcohol esters from 1-bromo-2-naphthoic acid in poor diastereoselectivity (13% ee).¹⁸ The diastereomeric ratio was improved to as high as 95% ee by converting 1-bromo-2-naphthoic acid into chiral oxazolines using readily available enantiopure amino alcohols, then coupling with copper. The corresponding 1,1'-binaphthyl-2,2'-dimethyl ester was generated by ring opening the oxazoline and esterification with sodium methoxy solution.¹⁹ The overall yield of the oxazoline precursor, was improved to 84% and asymmetric coupling was very successful.²⁰ Ito and co-workers were able to

asymmetrically synthesize 2,2'-dimethyl-1,1'-binaphthyl in up to 95% ee using a [(alkoxyalkyl)ferrocenyl]monophosphine/nickel catalyst.²¹

The lack of acidic or basic group on the monomer IV-6 itself precluded its direct chemical resolution via acid/base chemistry. Rather than trying to resolve the potential dicarboxylic acid intermediate in the synthesis of IV-6, thereby adding steps risking racemization, all efforts of chemical resolution were focused on the chemistry of the carbonyl unit. Two approaches were taken: a) formation of a Schiff base using a chiral amine and b) chiral reduction to form a chiral alcohol.

IV.5.2. Attempted Schiff Base Reaction

(+)-Methylbenzylamine, a readily available base, was selected in the attempted Schiff Base reaction with IV-6 (Scheme IV.7). Reagents such as *para*-toluene sulfonic acid and several Lewis acids (i.e. TiCl₄, DABCO, BF₃ etherate) were used to catalyze the reaction in a variety of solvents, but all efforts were unfruitful. In addition, hydrazine, phenyl hydrazine and semi carbizide were also tried.

Scheme IV.7. Attempted Schiff base reaction with monomer IV-6

IV.5.3. Attempted Asymmetric Reduction

Brown and co-workers found that (-)-diisopinocampheylchloroborane, or (-) DIP-Chloride, was able to reduce tertiary alkyl ketones with high enantiomeric excess.²² It was felt that reduction of a biaryl ketone like IV-6 was worth trying due to the availability of both (+) and (-) DIP-Chloride from Aldrich in bulk quantities. In addition, consideration of the molecular structure of IV-6 seemed to favor the formation of one diastereomer which would make isolation of stereoisomers more facile.

Scheme IV.8. Attempted asymmetric reduction of monomer IV-6

Attempts using high dilution with DMAc or CHCl_3 as a solvent, at room temperature, were unsuccessful (Scheme IV.8). It was believed that the ketone surrounded by two aryl groups, as in the case of IV-6, was too sterically hindered thus circumventing any success of reduction. Ultimately, all attempts of chemical resolution failed.

IV.5.4. Resolution by Chiral Chromatography

Resolution by chiral chromatography was attempted on monomer IV-6, binaphthalene-based model compound IV-7 and the [5]helicene model compound IV-10. Separation of enantiomers is possible by the interaction of π donor sites and π acceptors

sites of the stationary phase to complementary sites on the analyte as well as hydrogen bonding.

A mixture of 25% isopropanol in hexane, was used as the eluting solvent at room temperature with a flow rate of 2 mL/min. The UV detector was set at 254 nm. Two baseline resolved peaks were found for both the binaphthyl monomer, **IV-6** (RT= 33 and 51 min) and the model compound, **IV-7** (RT = 81 and 107 mins). The two peaks indicated the presence of two enantiomers thus providing a method to enantiomerically pure monomer **IV-6** which can be used for the synthesis of optically active polymers.

The [5]helicene model compound, **IV-10**, eluted much more quickly (RT = 12 mins) through the chiral column but with no separation. The retention time of the [5]helicene-based compound is much shorter due to the lack of ketone site which can interact more effectively with the stationary phase of the chiral column.

IV.6 Conclusions

A new route to the introduction of axial and helical chirality into poly(aryl ether)s was demonstrated by the design, synthesis and polymerization of a novel monomer, 2,2'-bis(4-fluorobenzoyl)-1,1'-binaphthalene. The unique synthetic approach was established using a known post-polymer transformation reaction¹⁰ and the 1,1'-binaphthyl poly(ether ketone) as a precursor. Insertion of the binaphthyl and [5]helical moieties resulted in increases in glass transition temperatures and decreases in decomposition temperatures over their equivalent biphenyl and phenanthracene-based polymers

This approach demonstrates the successful transformation from axial to helical chirality in poly(arylene ether)s. It was also found that the binaphthyl monomer (IV-6) can be resolved by chiral chromatography. Therefore, a method has been established, with the racemic series, which can eventually lead to the synthesis of optically active binaphthyl-based poly(aryl ether)s and their conversion to helicene-containing polymers. Although resolution with chiral chromatography is possible on a small scale, it would be more practical to find a method of chemical resolution for larger scale production of optically active starting monomer.

IV.7. Experimental Section

Materials

All the reagents were purchased from Aldrich with the exception of 1,2-dihydro-4-(4-hydroxyphenyl)(2H)phthalazin-1-one which was supplied by Prof. Xi-Gao of Dalian University of Technology in China. Tetrahydrofuran (THF) was dried by distilling over sodium metal for several days until it turned blue with benzophenone. Anhydrous N,N-dimethylacetamide was used directly. Nickel bromide (NiBr_2) and nickel chloride (NiCl_2) were dried for 48 hrs at 100 °C. Zinc powder (100 g) was washed with 2% HCl solution (2 x 250 mL), distilled water (3 x 85mL), 95% EtOH (2 x 170mL) and absolute EtOH (170 mL) before drying in a vacuum oven for 48 h/1mmHg) at room temperature.

For the polymerization reactions, reagent grade TMSO_2 was fractional distilled under vacuum (120°C/3 mmHg). Anhydrous potassium carbonate was ground in a crucible before use. BPA was recrystallized from toluene. Other reagents were used directly.

Measurements

The methods for characterization are same as those described in chapter two.

The Whelk-O 1 Chiral Stationary Phase (CSP) Pirkle-Concept HPLC column, supplied by Merck, was used for chiral separation liquid chromatography. The WHELK-O 1 CSP is made from covalently attaching 4-(3,5-dinitrobenzamido)tetrahydrophenanthrene to 3-propyl silica. 25% Isopropanol in hexane was used as the eluting solvent at room temperature with a flow rate of 2 mL/min. The UV detector was set at 254 nm.

Synthesis of 1-Bromo-2-bromomethylnaphthalene (IV-1)

A three-necked, 1 L round-bottomed flask fitted with a condenser was charged with 1-bromo-2-methylnaphthalene (100.00 g of 90% technical grade supplied by Aldrich, 0.452 moles), N-bromosuccinimide (85.54 g, 0.456 moles), benzoyl peroxide (0.40 g, 0.002 mole) and carbon tetrachloride (450 mL) under argon flow. After three hours of refluxing and stirring, TLC showed the reaction was complete. The succinimide by-product was filtered off after the reaction was allowed to cool to room temperature. The carbon tetrachloride was removed to give a beige solid which was recrystallized from cyclohexane and dried in vacuum oven overnight at 40 °C/1mmHg. Yield: 97.0 g (80%); m.p. 97-100°C. IR(KBr) cm^{-1} ; MS: EI (m/e , % relative intensity) 298 (M^+ , 7.7), 219 ($M^+ - \text{Br}$, 100.0), 140 ($M^+ - 2\text{Br}$, 61.2); ^1H NMR (400 MHz, CDCl_3) δ 8.29 (d, 1H, $J = 8.4$ Hz), 7.75 (m, 2H), 7.57 (m, 1H), 7.49 (m, 2H), 4.82 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 134.90, 134.12, 132.49, 128.26, 128.12, 127.81, 127.69, 127.59, 127.15, 124.92, 34.71.

Synthesis of (1-Bromo-2-naphthyl)methylalcohol (IV-2)

A 3L, three necked round-bottomed flask with mechanical stirrer in center neck and reflux condensers in side necks was set up in air atmosphere. Calcium Carbonate (102.60 g, 1.026 moles) was added, followed by distilled water (770 mL). A solution of 1-bromo-2-bromomethylnaphthalene (60.00 g, 0.200 moles) and 1,4-dioxane (770 mL) was then added. The solution was stirred and refluxed for 3 days. The dioxane and water was mostly removed (not to dryness! beware of peroxides!) and methylene chloride (750 mL) added. Dilute 3 M aqueous HCl was added slowly, to avoid foaming overflow, until all the solid had dissolved. The organic layer was separated, washed with NaHCO₃ (500mL), dried over MgSO₄ and filtered. After removing the organic layer, the solid was recrystallized from cyclohexane to give a white powder and dried in vacuum oven overnight at 40 °C/ 1mmHg. Yield 40.9 g (87%). m.p. 97-99 °C. IR(KBr) 3168 (O-H) cm⁻¹; MS (EI, *m/e*, % relative intensity) 236 (M⁺, 50.6), 157 (M⁺ - Br, 5.6) 128 (M⁺ - BrCOH, 100.0); ¹H NMR(400 MHz, CDCl₃) δ 8.20 (s, 1H), 7.80 (m, 3H), 7.54 (m, 1H), 7.31 (t, 1H, J = 7.7 Hz), 4.91 (s, 1H), 1.73 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 140.10, 134.21, 132.02, 130.24, 128.83, 127.75, 126.20, 125.99, 124.60, 122.82, 65.38.

Synthesis of 1-Bromo-2-naphthaldehyde (IV-3)

A solution of (1-bromo-2-naphthyl)methylalcohol (20.45 g, 0.087 mole) in methylene chloride (250 mL) was added to a 1-necked, 500 mL, round-bottomed flask

containing pyridinium chlorochromate (28.5 g, 0.132 mole) and methylene chloride (130 mL) in air atmosphere. The bright orange pyridinium chlorochromate turned black immediately upon addition of the alcohol. This was left to stir 18 hrs at room temperature. The reaction was poured out and anhydrous diethyl ether (400 mL) was added to rinse out the reaction flask. Both the washing and the reaction solution was filtered through a pad of Celite. More fresh anhydrous diethyl ether (100 mL) was used to flush any remaining aldehyde in the Celite pad. The filtered solution was roto-evaporated to dryness to give a brown residue which was recrystallized from cyclohexane to give white fine needles which was dried in a vacuum oven for one hour at 60°C/1mmHg: Yield 18.54 g (91%). m.p. 117-119 °C. IR(KBr) 1682 (C=O) cm^{-1} ; MS (EI, m/e : , % relative intensity) 234 (M^+ , 90.2), 205(M^+ - CHO, 24.4), 126 (M^+ - BrCHO, 100.0). ^1H NMR(400 MHz, CDCl_3) δ 10.60 (s, 1H), 8.42 (m, 1H), 7.85 (d, 1H, $J = 8.5$ Hz), 7.80 (m, 1H), 7.75(d, 1H, $J = 8.5$ Hz), 7.62 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 192.60, 137.09, 131.96, 131.21, 131.04, 129.61, 128.51, 128.16, 128.12, 127.98, 123.96.

Synthesis of (1-bromo-2-naphthyl)(4-fluorophenyl)methanol (IV-4)

A 1L, three necked round bottomed flask was set up with a condenser in the center neck, dry addition funnel on side neck and liquid addition funnel in the other side neck. Argon was allowed to flow in from the dry addition funnel and out through the condenser. Magnesium (3.61 g, 0.148 mole) turnings were added and then the glass apparatus was

flame dried. Dried tetrahydrofuran (55mL), 1-bromo-4-fluorobenzene (3.00 g, 0.017 mole) and a microspatula tip of iodine were added and heated to initiate the reaction giving rise to an orange/brown solution. The remaining 1-bromo-4-fluorobenzene (23.00 g, 0.131 mole) in solution with THF (40 mL) was added dropwise via the liquid addition funnel without heat until the refluxing subsided. The Grignard solution was stirred at room temperature for one hour to allow for complete reaction. When all the magnesium turnings had not dissolved, another 0.5 mL of 1-bromo-4-fluorobenzene was added. Again, not all the Mg dissolved, so the Grignard reagent was added to another flame-dried 500 mL, three necked round-bottomed flask to avoid any potential cross coupling in the presence of excess magnesium. In the second flask, 1-bromo-2-naphthaldehyde (31.87 g, 0.136 mole) was added slowly via the dry addition funnel. The reaction occurred immediately according to TLC and was poured into a 10% HCl (aq) solution to form an oily yellow layer. Methylene chloride was used to extract the product (2 x 250 mL) and the combined organics were washed with saturated NaHCO₃ (aq) solution and distilled water. The organic layer was then dried over MgSO₄, filtered and roto-evaporated to give a syrup which somewhat solidified overnight. Complete solidification resulted upon the addition of hexane to give white powder. Yield 38.54 g (86%). Recrystallization was needed for the next step. m.p. 103-105 °C, IR(KBr) 3380 (OH) cm⁻¹; MS (EI, *m/e*, % relative intensity) 330 (65.6, M⁺); ¹H NMR(400 MHz, CDCl₃) δ 8.31 (d, 1H, J = 8.5 Hz), 7.81 (m, 2H), 7.64 (d, 1H, J = 8.6 Hz), 7.60 (m, 1H), 7.52 (m, 1H), 7.42 (dd, 2H, J_{H-H} = 8.7 Hz, J_{H-F} = 5.4 Hz), 7.00 (t, 2H, J_{H-H} = 8.7 Hz), 6.55 (s, 1H), 2.07 (s, 1H); ¹³C NMR (100 MHz,

CDCl_3) δ 175.89, 163.41, 140.40, 138.18, 134.14, 133.0, 132.17, 128.52, 128.44, 128.28, 128.17, 127.63, 127.52, 126.82, 125.03, 122.62, 115.38, 115.17, 74.66.

Synthesis of 1-Bromo-2-(4-fluorobenzoyl)naphthalene (IV-5)

A 500 mL, round bottomed flask was charged with pyridinium chlorochromate (25.47 g, 0.118 mole) and methylene chloride (200 mL) in air atmosphere. In a separate flask, (1-bromo-2-naphthyl)(4-fluorobenzene)methanol (25.92 g, 0.079 mole) was dissolved in 200 mL CH_2Cl_2 and then added to the PCC/ CH_2Cl_2 slurry and stirred overnight. The reaction was diluted with diethyl ether, filtered through Celite, rotovapped, filtered and recrystallized from hexane/cyclohexane in a 50/50 mixture to give fine white needle which were dried in a vacuum oven overnight at $50^\circ\text{C}/1\text{mmHg}$. Yield 22.71 g (88%); m.p. $134\text{--}136^\circ\text{C}$; IR(KBr) cm^{-1} 1672 (C=O), 1596 (C=C aromatic); MS (EI, m/e , % relative intensity) 328 (M^+ , 52.1), 249 ($\text{M}^+ - \text{Br}$, 11.4), 233 ($\text{M}^+ - \text{PhF}$, 32.9), 123 (COPhF^+ , 100); ^1H NMR (400 MHz, CDCl_3) δ 8.35 (d, 1H, $J_{\text{H-H}} = 8.4$ Hz), 7.90 (m, 4H), 7.67 (m, 2H), 7.35-7.39 (d, 1H, $J_{\text{H-H}} = 8.3$ Hz), 7.12 (t, 2H, $J_{\text{H-H}} = 8.5$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 194.86, 167.46, 164.91, 138.47, 134.61, 132.98, 132.88, 132.64, 131.87, 128.40, 128.37, 128.31, 127.80, 127.44, 124.54, 119.78, 116.05, 115.83.

Synthesis of 2,2'-bis(4-fluorobenzoyl)-1,1'-binaphthalene (IV-6)

A 250 mL, three necked round bottomed flask was charged with zinc (2.90 g, 0.046 mole) and flame dried under argon flow. Triphenylphosphine (3.20 g, 0.012 mole) and NiCl_2 (0.40 g, 0.0012 mole) were added to the flask with anhydrous DMAc (40 mL) and stirred at 80 °c to generate the blood red catalyst. After an hour of stirring, a solution 1-bromo-2-(4-fluorobenzoyl)naphthalene (10.00 g, 0.031 mole) in DMAc (100 mL) was added slowly the reaction. After the reaction was seen to be completed by TLC, the DMAc was distilled off to leave a gray slurry. The slurry was rinsed with dichloromethane to leave a solid which was recrystallized with 1,2-dichlorobenzene to give a white powder. Yield 4.78g (63.0%): This can be sublimed to give white prismatic crystals. m.p. 298 °C. IR (KBr) cm^{-1} 1657 (C=O); MS (EI, m/e , % relative intensity) 498 (M^+ , 6.6), 375 ($\text{M}^+ - \text{COPhF}$, 100.0), 250 (Binaph^+ , 4.3), 123 (COPhF^+ , 12.8), 95 (PhF^+ , 18.0); Anal. Calcd for $\text{C}_{34}\text{H}_{20}\text{O}_2\text{F}_2$: C, 81.92; H, 4.04; O, 6.42; F, 7.62. Found: C, 81.57; H, 4.06; F, 7.89; UV/VIS (CHCl_3) λ_{max} 255 nm; ^1H NMR (400 MHz, 1:1 $\text{CF}_3\text{COOD}/\text{CDCl}_3$) δ 8.03 (d, 2H, $J_{\text{H-H}} = 8.6$ Hz), 7.97 (d, 2H $J_{\text{H-H}} = 8.3$ Hz), 7.61 (m, 8H), 7.42 (m, 4H), 6.80 (t, 4H, $J_{\text{H-H}} = 8.4$ Hz); ^{19}F NMR (300 MHz, CHCl_3) -106.3 ppm.

X-ray Structure Determination of Monomer IV-6

Crystal structure determination was performed by Dr. Gary Enright of the National Research Council at the Sussex Laboratories in Ottawa, ON, Canada. White cubic crystals of IV-6 was obtained when the monomer was sublimed at 298 °C. The crystal dimensions were 0.12 mm X 0.15 mm X 0.15 mm. For $Z = 4$ and $FW = 498.52$, the calculated density is 1.415 mg/cm^3 . The intensity data were collected on a Siemens diffractometer using the omega- 2θ scan technique to a maximum value of 57.5. The space group was found to be monoclinic, $C 2/c$. Cell dimensions were obtained from 8000 reflections with 2θ angle in the range of 3.00 to 57.50 degrees. The cell dimensions were $a = 15.8933 (5) \text{ \AA}$, $b = 11.5883 (30) \text{ \AA}$, $c = 14.0788 (5) \text{ \AA}$, $\beta = 115.521$. The residuals are as follows: for significant reflections, $R_f = 0.048$, $R_w = 0.039$; for all reflections, $R_f = 0.072$, $R_w = 0.042$. A total of 8031 reflections were collected of which 3040 were unique. No corrections were made for absorption. Calculations were performed using the NRCVAX crystallographic software package.

Synthesis of Ether Model Compound (IV-7)

Monomer IV-6 (1.000 g, 2.01 mmol), 4-*tert*-Butyl phenol (0.603 g, 4.02 mmol) and K_2CO_3 (0.88g, 637 mmol) were added to a three-necked round bottom flask which was previously flame dried under argon flow. $TMSO_2$ (4 mL) and chlorobenzene (4 mL) were added and the reaction mixture was heated to 140°C to azeotrope water off for one hour. The temperature was then increased to 200 °C and maintained for three hours at which time TLC showed the reaction was complete. The reaction mixture was precipitated

into a 50/50 (v/v) solution of methanol/water containing a few drops of concentrated HCL. The solid was filtered to form a white paste which after drying overnight in a vacuum oven at 40°C/5mmHg formed a glassy white solid. Yield: 1.35g (89%); m.p. 125-135 °C. IR(KBr) cm^{-1} 1664 (C=O); MS (FAB, m/e , % relative intensity) 759 ($M^+ + H$, 8.1); UV/VIS (CHCl_3) λ_{max} 295 nm; ^1H NMR (400 MHz, CDCl_3) δ 7.93 (d, 2H, $J_{\text{H-H}} = 8.3$ Hz), 7.91 (d, 2H, $J_{\text{H-H}} = 8.5$ Hz), 7.53 (m, 2H), 7.49 (d, 2H, $J_{\text{H-H}} = 8.5$ Hz), 7.38 (d, 4H, $J_{\text{H-H}} = 8.9$ Hz), 7.37 (d, 4H, $J_{\text{H-H}} = 8.8$ Hz), 7.30 (m, 4H), 6.95 (d, 4H, $J_{\text{H-H}} = 8.8$ Hz), 6.58 (d, 4H, $J_{\text{H-H}} = 8.9$ Hz), 1.32 (s, 18H); ^{13}C NMR (100 MHz, CDCl_3) δ 195.74, 161.91, 152.68, 147.60, 136.50, 136.04, 134.28, 133.54, 132.46, 131.39, 128.27, 128.04, 127.32, 127.15, 126.88, 126.84, 125.39, 119.88, 115.95, 31.59, 31.45.

Polymer Synthesis (IV-8a, IV-8i)

To a 50 mL round bottomed flask, equipped with Dean Stark trap and previously flame dried under a nitrogen flow, was added 2,2'-bis(4-fluorobenzoyl)-1,1'-binaphthalene (1.494 g, 3.0 mmol), bisphenol A (0.685 g, 3.0 mmol) and crushed K_2CO_3 (0.749 g, 5.4 mmol). Tetramethylenesulfone (5.4 mL) (40% g/mL) and chlorobenzene (4 mL) were then added and the solution was heated to 160 °C while water was removed via its azeotrope with chlorobenzene. After 45 min, the solution was heated to 200 °C for polymerization to occur. The reaction was stopped when GPC monitoring failed to show an increase in molecular weight (4 hrs in total). The reaction was poured into a stirring solution of methanol (200 mL) containing a few drops of concentrated HCL which precipitated a stringy white polymer. The polymer was decanted and redissolved in

chloroform (100 mL) and filtered through Celite to remove any remaining inorganic salts. This was then reverse precipitated; a small amount of MeOH (up to 50 mL) was added to the larger amount of polymer/chloroform solution to form a gummy ball. The gummy ball was decanted, then redissolved in a small amount of chloroform (25 mL) and reprecipitated into methanol (150-200 mL) to form a white, fluffy material. The polymer fibers were filtered and then stirred in fresh boiling methanol to remove any remaining oligomers, filtered again and dried in a vacuum oven overnight at 170°C/5mmHg; Yield of Polymer IV-8a (after reverse precipitation) was 1.2 g (58%); IR(film) 1664 (C=O) cm^{-1} ; UV (CHCl_3) λ_{max} 294 nm; ^1H NMR (400MHz, CDCl_3) δ 7.91 (d, 2H, $J_{\text{H-H}} = 8.5$ Hz), 7.88 (d, 2H, $J_{\text{H-H}} = 8.7$ Hz), 7.51 (m, 2H), 7.48 (d, 2H, $J_{\text{H-H}} = 8.5$ Hz), 7.41 (d, 4H, $J_{\text{H-H}} = 8.7$ Hz), 7.31 (m, 4H), 7.21 (d, 4H, $J_{\text{H-H}} = 8.6$ Hz), 6.91(d, 4H, $J_{\text{H-H}} = 8.6$ Hz), 6.59 (d, 4H, $J_{\text{H-H}} = 8.8$ Hz), 1.67 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 195.71, 161.50, 153.09, 146.75, 136.36, 136.06, 134.10, 133.54, 132.38, 131.66, 128.27, 128.21, 128.02, 127.37, 127.17, 126.87, 125.41, 119.72, 116.17, 42.32, 31.01.

Polymer IV-8i: Instead of using K_2CO_3 as the base, Cs_2CO_3 was used in conjunction with $\text{Mg}(\text{OH})_2$ according to the procedure by Hay.¹⁵ Yield 63% (after reverse precipitation); IR (KBr, cm^{-1}) 1669 (C=O), 1240 (C-O) ; UV (CHCl_3 , nm) λ_{max} 264, 295.

Transformation of Monomer and Model Compound (IV-9, IV-10)

A typical procedure is as follows: A 50 mL, three necked round-bottomed flask was flame dried under argon flow and charged with monomer (IV-6) (0.50g, 1.00 mmol),

15 mL of TCE and Lawesson reagent (0.81 g, 2.00 mmol). The reaction mixture was stirred and heated to 120°C. Within 10 min the reaction turned a light lime green color, then a dark green/blue color within 20 min, followed by an aqua marine blue by 30 mins. Two hours later, IR showed a significant reduction of the ketone peak but the reaction was left to stir/heat overnight to effect full transformation on the monomer. 24 h after the reaction started, IR showed the complete disappearance of the ketone peak and TCE is distilled from the reaction mixture. The remaining product was washed several times with methanol before boiling in methanol for 3 hrs to form a blue/white solid (IV-9): Yield: 0.35g (74%); Mp >300 °C; IR (KBr) 1592 cm⁻¹ (C-C aromatic); MS (EI, *m/e*, % relative intensity) 466 (M⁺, 100.0), 375 (M⁺ -PhF, 75.9), 276 (M⁺ -2PhF, 8.6); ¹H NMR (400 MHz, CDCl₃) δ 8.45 (d, 2H, J_{H-H} = 10.9 Hz), 7.94 (d, 2H, J_{H-H} = 7.8 Hz), 7.82 (d, 2H, J_{H-H} = 8.9 Hz), 7.53 (m, 2H, J_{H-H} = 8.8 Hz), 7.51 (m, 2H), 7.28 (m, 2H), 7.15 (m, 2H), 7.08 (m, 2H), 6.98 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 161.65 (¹J_{C-F} = 244 Hz), 137.07, 135.15, 133.60 (³J_{C-F} = 8 Hz), 132.23 (³J_{C-F} = 7 Hz), 132.06, 130.95, 130.58, 129.53, 127.67, 127.40, 126.82, 126.54, 124.75, 124.43, 114.83 (²J_{C-F} = 21 Hz).

Model Compound IV-10: White powder; Yield 0.27g (70.2%); Mp 283-285°C; IR (KBr) no carbonyl seen at 1664 cm⁻¹; UV (CHCl₃) λ_{max} 268, 315 nm; Fluorescence (CHCl₃) λ_{em} 435 (excitation: 315 nm); ¹H NMR (400 MHz, CDCl₃) δ 8.46 (d, 1H, J_{H-H} = 8.5 Hz), 7.93 (d, 1H, J_{H-H} = 7.9 Hz), 7.85 (d, 1H, J_{H-H} = 8.9 Hz), 7.69 (d, 1H, J_{H-H} = 8.9 Hz), 7.51 (t, 1H, J_{H-H} = 7.4 Hz), 7.35 (d, 2H, J_{H-H} = 8.7 Hz), 7.27 (t, 1H, J_{H-H} = 7.7 Hz), 7.14 (d, 1H, J_{H-H} = 8.3 Hz), 7.09 (d, 1H, J_{H-H} = 8.3 Hz), 6.94 (m, 4H), 1.33 (s, 9H); ¹³C NMR (100

MHz, CDCl₃) δ 156.05, 154.89, 146.00, 137.71, 134.20, 132.96, 132.13, 132.03, 131.05, 130.62, 129.52, 127.63, 127.21, 126.66, 126.54, 126.36, 124.72, 124.60, 118.20, 118.10, 34.29, 31.50.

Polymer Transformation (IV-11)

The diketone polymer **IV-8** (0.343 g, 0.5 mmol) was added to a 50 mL, flame dried, round bottomed flask and dissolved with tetrachloroethane (10 mL) under argon flow. Lawesson's reagent (0.405 g, 1.0 mmol) was added and the reaction mixture quickly turned cloudy, light yellow. As the mixture was heated to 120 °C the solution turned a clear light green color and was left stirring overnight at 120 °C to form a clear, dark yellow color the next day. Most the TCE was removed by vacuum distillation using a water aspirator (i.e. down to 0.5 - 1.0 mL). The remaining slurry was precipitated into methanol to form a powder and was stirred. The powder was filtered and washed with methanol again. The resulting polymer was dissolved in chloroform and precipitated in methanol and dried overnight in a vacuum oven (100 °C, 1 mmHg); Yield 87%; IR(KBr) 1596 (C-C aromatic) cm⁻¹; UV (CHCl₃) λ_{max} 268, 315 nm; Fluorescence (CHCl₃) λ_{em} 435 (excitation: 315 nm); ¹H NMR (400 MHz, CDCl₃) δ 8.41 (d, 2H, J_{H-H} = 8.5 Hz), 7.84 (d, 2H, J_{H-H} = 7.9 Hz), 7.74 (d, 2H, J_{H-H} = 8.9 Hz), 7.62 (d, 2H, J_{H-H} = 8.9 Hz), 7.44 (t, 2H, J_{H-H} = 7.4 Hz), 7.19 (m, 6H), 7.06 (d, 2H, J_{H-H} = 8.2 Hz), 7.01 (d, 2H, J_{H-H} = 8.2 Hz), 6.87 (m, 8H), 1.60 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 155.76, 155.09, 145.40, 137.60, 134.28, 132.93, 132.09, 131.97, 130.99, 129.46, 128.01, 127.59, 127.20, 126.63, 126.34, 124.63, 124.58, 118.18, 118.08, 42.06, 31.06.

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Summary

A series of ketone and sulfone activated dihalo aryl monomers were synthesized containing a 1,4-naphthylene moiety. The enhanced reactivity of the naphthyl portion of the ketone monomer towards nucleophilic polymerization over its phenyl counterpart was predicted by HMO calculations and Meisenheimer complex considerations. Polymerization of four dihaloaryl ketone monomers with four different bisphenols demonstrated the poor reactivity of the chlorophenyl portion in the BPA case. Model studies showed evidence of an *in-situ* halogen reaction but was found to play a minimal role during the polymerization conditions due to its slow rate. Copolymerization showed high molecular weight polymers could be made with ratios as low as 1:4 of the difluoro to dichloro ketone monomers with BPA.

Polymerization with a series of eight bisphenols and one heterocyclic monomer resulted in two new series of poly(aryl ether ketone)s (PAEK) and poly(aryl ether sulfone)s (PAES). In all cases, 1,4-naphthylene insertion served to increase the stiffness of the polymer backbone (as seen by increases in T_g), reduce crystallinity and improve gas permselectivity while lowering gas permeability. The use of the heterocyclic monomer, 1,2-dihydro-4-(4-hydroxyphenyl)(2H)phthalazin-1-one, resulted in polymers with the highest glass transition temperatures for both series. ($T_g = 317\text{ }^{\circ}\text{C}$ for PAES and $T_g = 290\text{ }^{\circ}\text{C}$ for PAEK). Whereas the 1,4-naphthylene-based PAES series exhibited higher T_g than the equivalent PAEK, the decomposition temperature for 5% weight loss of the PAEK series were higher than their PAES counterpart.

A unique binaphthalene-containing difluoro ketone monomer was designed, synthesized and polymerized with BPA (T_g of 225 °C) and the above heterocyclic monomer (T_g of 287 °C). The binaphthyl-based BPA polymer precursor was subjected to a transformation reaction which introduced a [5]helicene unit into its main chain. The helicene-based polymer had a T_g of 265 °C and T_d of 459 °C. This demonstrated the first example of incorporation of axial and helical chirality into poly(aryl ether)s. Attempts to chemically resolve the racemic binaphthyl monomer failed but it was shown that chiral chromatography could separate the monomer into its two enantiomeric forms.

IMAGE EVALUATION TEST TARGET (QA-3)

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