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**THE SYNTHESIS AND PROPERTIES OF NAPHTHALENE-BASED
POLY(ARYLENE ETHER KETONE)S**

BY

PETER WILLIAM BROUGHTON, B.Sc.

**A thesis submitted to
the Faculty of Graduate Studies and Research
in partial fulfillment of the requirements for the degree of
Masters of Science**

The Department of Chemistry

**Carleton University
Ottawa, Ontario, Canada
September 1995**

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**THE SYNTHESIS AND PROPERTIES OF NAPHTHALENE-BASED
POLY(ARYLENE ETHER KETONE)S**

submitted by

PETER WILLIAM BROUGHTON, B.Sc.

in partial fulfillment of the requirements
for the degree of Masters of Science

Prof. Z. Y. Wang, Thesis Supervisor

Prof. J. S. Wright, Chair, Department of Chemistry

Carleton University

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Abstract

In studying the correlations of structure to polymer properties, several moderate to high molecular weight amorphous and semicrystalline poly(arylene ether ketones) were synthesized from 1,4-bis(4'-fluoro-1'-naphthoyl)benzene and 4-chloro-1-(4'-fluoro-1'-naphthoyl) naphthalene with a variety of bisphenols. The polymers were characterized by high resolution ^1H and ^{13}C NMR, solution viscosity, as well as gel permeation chromatography. Glass transition temperatures, measured by differential scanning calorimetry (DSC), ranged from 205 °C to 273 °C. Although only one T_m (crystallization melting point) was observed for polymer III-1c prepared in DPS, no appreciable crystallinity was found in polymers (III-1c,d and III-2c,d) prepared in N-methylcaprolactam, which was confirmed by Wide Angle X-ray Scattering. No observable crystallization was detected by DSC. The 5% weight loss of polymers as assessed by thermogravimetry occurred all above 480 °C in nitrogen and 430 °C in static air.

The naphthalene moiety increases the T_g as they are incorporated into the backbone structure of poly(aryl ether ketone)s, but decreases the value of T_m , thus giving a higher ratio of T_g to T_m . Moreover, the twisted conformation due to the bulky naphthyl rings, in most cases, prevents the effective crystallization, thus giving rise to amorphous polymers.

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SYMBOLS AND ABBREVIATIONS

BPA	Bisphenol A or 4,4'-Isopropylidenediphenol
6F-BPA	4,4'-hexafluoroisopropylidenediphenol
Cl-naph	Chloronaphthalene
COSY	Correlated Spectroscopy
DMAc	N,N-dimethylacetamide
DMF	N,N-dimethylformamide
DMSO	Dimethyl sulfoxide
DPS	Diphenyl sulfone
DSC	Differential Scanning Calorimetry
E'	Young's modulus
EtOAc	Ethyl acetate
GPC	Gel Permeation Chromatography
HETCOR	Heteronuclear shift correlation
HRMS	High resolution mass spectrometry
IR	Infrared
J	Coupling constant (Hz)
MS	Mass spectrometry
Mn	Number average molecular weight
Mw	Weight average molecular weight
n	Number of polymer repeat units
N ₂	Nitrogen
NMP	N-methylpyrrolidinone
NMR	Nuclear magnetic resonance
PEEK	Poly(ether ether ketone)
PES	Poly(ether sulfone)
S _N Ar	Nucleophilic aromatic substitution
Tan δ	Loss tangent
Td	Decomposition temperature
Tg	Glass transition temperature
TG	Thermogravimetry
TLC	Thin layer chromatography
Tm	Crystalline melting point
TMA	Thermomechanical analysis
TMSO ₂	Tetramethylene sulfone
δ	Chemical shift (ppm)

η_{inh}	Inherent viscosity
η_{int}	Intrinsic viscosity
WAXS	Wide angle X-ray scattering

CHAPTER 1. Introduction

When describing the desirable properties of a fiber, a rubber, or a plastic, one would most likely include high tensile strength, resistance, toughness, and depending on the application, thermal and weather resistabilities respectively. Because of properties such as these that make polymers commercially useful, characterization can be considered to be without a doubt, the most important aspect of polymer chemistry. While systematic studies of synthesis and properties, including the development of technologically useful materials did not start until the 1950's, high-performance thermoplastics such as poly(arylene ether ketones) have recently shown great potential for uses in high-performance systems such as advanced aircraft and space industries. The desirability of the said materials stems from the outstanding thermal (usable at temperatures up to 500 °C for prolonged periods) and mechanical (toughness) properties.

Thermally stable polymers exhibit high melting and softening points for amorphous and crystalline polymers, low weight loss at elevated temperatures, and inertness to chemical attack, oxidation, and moisture¹. The composition of materials displaying high thermal stabilities usually incorporate as a major part of the polymer composition, an aromatic or other thermally unreactive ring structure and a highly resonance-stabilized system.

When determining the heat resistance of a polymer, the strength of the primary bonds, especially those in the backbone structure, is without a doubt, the single most important determinant². Commercial poly(p-phenylene) is a great example as it is stable up to 660 °C without sustaining any weight loss, and exhibits a T_m of 530 °C.

Figure I.1. Structure of poly(p-phenylene)

Because of its high melting point and degree of crystallinity, it is impossible to be melt or solution processed which inevitably restricts the processability and commercial

usefulness of these high-temperature polymers. Therefore, the introduction of such functionalities as ethers, amides, and sulfones into the polymer backbones has been studied to improve solubilities and processabilities of these heat-resistant polymers.

1.1 Poly(arylene ether ketone)s

Poly(arylene ether ketone)s comprise a class of polymers in which arylene groups are linked together by carbonyl and ether moieties. Since the earlier investigations into poly(ether ketones), materials such as "Astrel-360" (poly ether sulfone)³, "Udel" (polysulfone)³, and "Victrex" PEEK⁴ have emerged as high-performance engineering thermoplastics.

Figure 1.2. PES, Udel, and PEEK Polymers

The combined physical, chemical, and mechanical properties of these materials have led to their uses in a variety of applications such as toughening agents, adhesives, coatings, and molding components^{5,6}.

A characteristic difference between poly(ether sulfone)s and poly(arylene ether ketone)s is the tendency for the latter class of polyethers to crystallize. Most of

Poly(arylene ether ketone)s, being crystalline, can exhibit melting point temperatures up to 450 °C, while in the amorphous state, show T_g values up to 230 °C^{7,8}.

The poly(arylene ether ketone) that has received the most attention is ICI's PEEK (Figure 1.1) This material, first commercialized in the early 1980's, exhibits good dielectric properties as well as chemical resistance at elevated temperatures and is being widely used in electrical, automotive, and aeronautical applications⁴.

Poly(arylene ether ketone)s, contrary to amorphous poly(arylene ether sulfone)s, are usually crystalline and therefore can resist attack of most solvents. This is markedly important when they are used in the aerospace environment, as is commonly the case. The only common room temperature solvent known for Poly(ether ketone) (PEK) and PEEK is concentrated sulfuric acid⁴.

1.2. Polymer Morphologies

Solid polymers differ from ordinary, low molecular weight compounds in the nature of their physical state or morphology but how does the physical state of the polymer relate to the morphology? Generally, two morphologies are characteristic of polymers - *amorphous* and *crystalline*. These terms are used to indicate in the case of the former, an almost complete lack of order among the molecules, while in the latter, molecules which are aligned, or oriented in a regular array, analogous to that of crystal lattice packing in non polymeric materials. Different polymers exhibit differing degrees of this behavior. The known polymers constitute a spectrum of materials ranging from those that are completely amorphous to those which possess low, to moderate, to high crystallinity. Crystalline polymers are, however, never 100% crystalline due to the amorphous portions invariably persisting in the spaces between the crystalline regions⁹.

1.2.1 The amorphous state - Rheology

The amorphous state is characteristic of those polymers in the solid state that, for reasons of structure, exhibit no tendency toward crystallinity. Within this rheology, there exists two amorphous states, solid and liquid, that differ in molecular motion. In the former, motion is restricted to short range vibrations and rotations provided the polymer retains its glass-like structure. With the latter, there is considerable conformational freedom arising from the rotation about the chemical bonds¹⁰. It is when an amorphous polymer receives a certain degree of rotational freedom that it can be deformed.

One of the most important characteristics of the amorphous state is the behavior of the polymer during its transition from a solid to a liquid. When the amorphous glass is heated, the kinetic energy of the molecules increase. This motion is restricted to short range vibrations and rotations provided the polymer retains its glass-like structure. As the temperature is increased further, there comes a point where a change takes place; the polymer loses its glass-like properties and assumes those completely associated with a rubber. The temperature at which this takes place is the *glass transition temperature* (T_g).

Given that T_g is a function of rotational freedom, chemical structure is clearly the most important factor in the determination of this thermal property. Therefore, whatever restricts the rotation of the polymer backbone should invariably increase the T_g . Other factors would include aging (oxidation and exposure to UV light), differences in measurement methods (thermal vs mechanical), and molecular weight. Although T_g is independent of molecular weight when it is substantially high, as the molecular weight decreases, so does T_g . As there are so many variables that affect the values of T_g , it is regarded as an approximation only.

Although T_g is associated with changes occurring in the disordered regions of the polymer, the effects of crystallinity on this transition have been well documented. The tendency for polymers to be crystalline increases with increasing stereoregularity in the

polymer backbone. Evidence¹² suggests that syndiotactic polymers - those polymer having alternating chiral centers of the same configuration - exhibit higher Tgs than isotactic polymers - polymers with each chiral center having the same configuration.

Tg is one of the fundamental properties as it relates to polymer properties and processing. There are many dramatic changes that can occur during this transition (enthalpy, modulus or stiffness, refractive index, and thermal conductivity) and as a result, Tg can be observed by several means¹¹, including dilatometry, dielectric and thermal measurements, and dynamic mechanical spectroscopy (DMS).

1.2.2 The crystalline state- Rheology

The phenomenon of crystallinity generally occurs in regions of the polymer matrix that order themselves in a thermodynamically favorable alignment. Generally, crystallinity can be expected if the polymer backbone is built up by para-linked unsubstituted benzene rings. Crystallization is, however, suppressed upon the addition of sp³-hybridized atoms such as the central carbon atom of a BPA molecule or a sulfonyl group. While methyl groups may slow the rate of crystallization, yet not preventing it, larger space filling functional substituents such as phenyl groups tend to completely suppress this phenomenon. Crystalline polymers are generally tougher, stiffer, more resistant to solvents, and higher in density than their amorphous counter parts.² The higher the degree of crystallinity, the more pronounced the properties. They have superior mechanical properties and solvent inertness which is a reflection of the greater cohesive strengths arising from the more effective internal forces among the closely packed array of molecules.

Although crystallinity may not be initially apparent, it can be induced in a number of ways: the cooling of molten polymers, annealing, and drawing - a process that removes any "kinks" from the polymer chain, extending them along a common axis promoting closer packing.

Unlike amorphous materials which soften over a broad range above the T_g , crystalline polymers melt over a narrow range which is observed most conveniently by thermal analysis, and is known as the *crystalline melting temperature* (T_m). Because the magnitude of T_m and T_g are governed by the same intermolecular forces, these values should parallel one another to an extent. T_g 's are roughly one half to two thirds the value of the corresponding T_m , when given in Kelvin¹.

1.3. Synthesis of Poly(arylene ether ketones)

The synthesis of poly(arylene ether ketone)s mainly involves the nucleophilic displacement of activated arom: 'c halides in polar solvents by alkali phenoxides or by Friedel-Crafts methods using Lewis acids with acid chlorides and/or phenoxy groups. While crystallinity offers poly(arylene ether ketone)s a unique set of properties among thermoplastics, it is this property, coupled with melting points generally above 300 °C¹³ that makes the synthesis so difficult. The problem herein lies in the task of keeping the polymers in solution so as to obtain high molecular weights. One method of doing this is working in a strong acidic media⁴ (the 'electrophilic' process) in which the carbonyl moieties are protonated. A second is working at very high temperatures (the 'nucleophilic' process) thus allowing the polymer to be solvated.

1.3.1 Electrophilic substitution polycondensation

The first successful approach to a completely aromatic poly(ether ketone) was investigated in the early 1950's by Bonner^{13,14,15} who utilized the Friedel-Crafts polyacylation. Monomers such as acid chloride and/or phenoxy groups can be condensed in the presence of Lewis Acids such as aluminum chloride or borontrifluoride (scheme 1.1).

Scheme I.1. Friedel-Crafts Polyacylation Reaction

The mechanism of Friedel-Crafts polycondensation is thought to operate on the basis that the attacking species is the acyl cation (or acylium ion) on the reactive phenyl groups (scheme I.2)

Scheme I.2. Mechanism for Electrophilic Substitution

It was found that when Friedel-Crafts polyacylations were conducted in solvents such as dichloromethane, carbon disulfide, and nitrobenzene, the oligomers prematurely

crystallized out of solution preventing attainment of high molecular weights^{15,16}. However, when these polycondensations were carried out in HF (with a BF_3 catalyst), high molecular weight poly(ether ketone)s were obtained. It was therefore believed that using Lewis Acid-catalyzed complexes, which were soluble, could produce high molecular weight polymers. The reacting acid chloride, in the presence of Lewis bases (usually DMF, n-butyronitrile, tetramethylammonium chloride, and lithium chloride) has yielded a number of high molecular weight materials (scheme I.3)¹⁷.

Scheme I.3. Lewis Acid Catalyzed Polymerization

Another approach to Friedel-Crafts polycondensation utilizes the solvating power and catalytic activity of trifluoromethanesulfonic acid (triflic acid). This super acid catalyzes the synthesis of aromatic ketones from acid chlorides at room temperature¹⁸ and also the preparation of poly(ether ketone)s at moderate temperatures¹⁹.

There are two inherent problems associated with the Friedel-Crafts polycondensation method for the synthesis of poly(arylene ether ketone)s. First, branching can occur as a result of acylation in the ortho position and second, the use of expensive, aggressive, and poisonous reaction medium. Nonetheless, Friedel-Crafts polycondensation reactions remain an integral part of synthetic polymer chemistry.

I.3.2 Nucleophilic displacement polycondensation

The polymerization process by nucleophilic displacement that was originally developed for polysulfones²⁰ has been successfully adapted by ICI for the production of poly(arylene ether ketone)s. The aromatic nucleophilic substitution reaction (scheme I.4) that produces poly(arylene ether ketone)s is considered to proceed through an S_NAr mechanism^{21,22}.

Scheme I.4. S_NAr Mechanism Of Aromatic Nucleophilic Substitution

The reaction employs the polycondensation of alkali salts with dihalogenated (chloro- and fluoro-) ketones. The essential features in this reaction are the use of aprotic solvents and the activation of the halide by electron withdrawing groups in the ortho and para positions.

The first experiments conducted with 4,4'-dichloro or 4,4'-difluorobenzophenone in DMSO demonstrated the dichloro adduct was not reactive enough to yield high molecular weight polymers¹³ where the difluoro adduct was. However, these low molecular weights were not solely due to the decreased activity with respect to the bis(aryl fluorides)²¹. Reductive elimination, which is determined by the nature of the solvent as well as the reaction temperature, may also play a role²¹.

The nature of the reaction (i.e., electron withdrawing group, the halide, the cation, and the solvent) all have a marked influence on the course of the reaction. The power of the electron withdrawing group lies in the order $\text{SO}_2 \approx \text{NO}_2 > \text{C}=\text{O} > \text{N}=\text{N}$; for the halogens, $\text{F} \gg \text{Cl} > \text{Br} > \text{I}$; and for the metal cations, $\text{Cs} > \text{K} > \text{Na} > \text{Li}$. The choice of solvent can be complicated, with dimethylsulfoxide (bp: 180 °C) being favored for polymers which will form and remain in solution below 170 °C.

Crystalline poly(arylene ether ketone)s generally require a high boiling solvent; diphenylsulfone (DPS) is a favored example. However, the high reaction temperatures required for the dissolution of crystalline polyether ketones have the disadvantage that side reactions (i.e., cross-linking) may occur, even though polyether ketones, once prepared, are thermally stable up to temperatures above 400 °C. A successful approach incorporating the ketalization of 4,4'-dihydroxybenzophenone avoided these side reactions by lowering the reactive temperatures has been studied,²³ generating crystalline poly(arylene ether ketone)s with high melting points ($T_m = 370\text{-}372$ °C). Nonetheless, this approach has shortcomings: first, it is limited to few monomers, and second, it is presumably too expensive due to the high cost of monomers.

I.4. Rationale of Research

It has been well documented²¹ that the most popular method of synthesizing poly(arylene ether ketones) is by nucleophilic displacement of bisphenoxides and activated dihaloaryl ketones. The success in attaining high molecular weight poly(arylene ether ketones) is in part due to the use of reactive dihalide monomers that are able to form stable Meisenheimer complexes. For many known monomers containing 4-halophenyl end groups (i.e., 4,4'-dihalo benzophenone),²⁴ the Meisenheimer complex has only one main resonance form (Figure I.3). The possibility of different benzenoid moieties that could offer further resonance stabilization to the Meisenheimer intermediate poses interesting scenarios. Naphthalene is an obvious choice.

Figure I.3. Stable Meisenheimer Complex of 4,4'-difluorobenzophenone

Recent work²⁴ has shown a distinct increase in the physical and mechanical properties of poly(arylene ether ketone)s upon the addition of one naphthalene moiety to the PEEK analogue forming an unsymmetric dihaloaryl system. Would the addition of two naphthyl moieties have the same positive effects (Figure I.4) or would the added bulky nature of the second group hinder the process?

Figure I.4. Synthetic Analogues

	T _g °C	T _m °C
	143	334
	188 ²⁴	-
	Higher T _g ?	T _m ?

Therefore, two dihalodinaphthyl systems (Figure I.5) were synthesized to investigate their polymerizability, their physical, and their mechanical properties in comparison to the well known PEEK and other analogues.

Figure I.5. Synthetic Target Monomers

Some of the problems associated with attaining high molecular weight polymers lies in the purity of the monomers as well as the reactivities of these monomers with the bisphenols used. Although analytical methods such as HPLC may give some indication as to the purity of the monomers, the only definitive method for finding this is in doing a polymerization. Often, a model reaction is carried out to determine whether or not the monomer is reactive enough for nucleophilic displacement reactions. However, in light of the current studies being carried out on similar naphthalene-based systems²⁴ and their inherent reactivities to the bisphenols used, this procedure was not done.

In the past, techniques of NMR and MS have helped in the indication of sample purity. Traditionally, the melting temperatures were the main criterion for purity, giving indication by the sharpness or broadness of the range. DSC has now become a standard method for purity determination. Heats of melting are readily determined, and the initial shape of the melting curve can give an indication of how pure the sample is. DSC has rendered techniques such as mixed melting temperatures and melting temperature depressions obsolete.

CHAPTER II. Synthesis of monomers

The Friedel-Crafts acylation pathway was studied for the synthesis of both target monomers: [I-] & [I-2] (scheme II.1a and b). In both instances, inexpensive and readily available starting materials were utilized. For the synthesis of [I-1], terephthaloyl dichloride was reacted with fluoronaphthalene via a double Friedel-Crafts electrophilic substitution reaction. For the synthesis of [I-2], 4-chloro-1-acetonaphthone was produced by the simple acylation of acetyl chloride and 1-chloronaphthalene. This product was transformed to the acid via oxidation with sodium hypochlorite, which, in turn, was converted to the acid chloride with SOCl_2 , PCl_3 , or PCl_5 ²². The desired monomer [I-2] was then obtained with the Friedel-Crafts acylation of the acid chloride with the appropriate halogenated naphthalene.

Scheme II.1a. Synthesis of 1,4-bis(4'-fluoro-1'-naphthoyl)benzene

Scheme II.1b. Synthesis of 4-chloro-1-(4'-fluoro-1'-naphthoyl)naphthalene

II.1 Friedel-Crafts Acylation

It has been found that the single most important method for the preparation of naphthyl ketones is the Friedel-Crafts reaction²⁵. Friedel-Crafts acylation of aromatics is of considerable practical value, owing to the synthesis of such acyl ketones as aceto- and benzophenone. This ketone synthesis implies the introduction of the acyl group into the aromatic nucleus upon the action of an acylating agent, usually an acyl halide, anhydride, ester, or the acid itself, in the presence of a Friedel-Crafts catalyst. Lewis acids such as aluminum chloride and borontrifluoride are most commonly used as catalysts. A little more than one equivalent is required per mole of reagent as the first mole coordinates with the oxygen of the reagent²⁶ giving a 1:1 addition product (Figure II.1), which then acts as the active acylating agent.

Figure II.1. Friedel-Crafts 1:1 addition complex

As it is clear that the function of the Lewis acid is to polarize the acylating agent so as to increase the electrophilicity of the acyl cation, there is controversy about the exact nature of the acylating entity. That is whether it is the entity given in Figure II.1. or, in fact, the acylium ion. Indeed, it is likely that both are acylating agents, the more effective one in a given case being determined by the conditions of the reaction²⁷. For example, it is very probable that the acylium ion is the significant species in acylations using acid anhydride in sulfuric acid. On the other hand, acylations are often conducted in non-polar solvents which would not easily accommodate a high energy cation, and acylium ions are not detectable in these solvents. Under these circumstances, it is suggested that polarized complexes (Figure II.1.) are responsible for acylations. This is

supported by the observation that the benzoylation of toluene with benzoyl chloride catalyzed by aluminum chloride in nitrobenzene gives only 7% of the ortho derivatives²⁷. This can hardly be attributed to the simple acylium ion, whose steric requirements should be no greater than those of the isopropyl cation, which gives 26% ortho-substituted product, and therefore the polarizing complex is the acylating species.

With the acylations of aromatic systems, it is generally difficult to introduce more than one acyl group into the nucleus as RCO is a deactivator²⁶. This is due to the fact that the acyl group first introduced is present in the reaction media as the aluminum chloride (or related acid catalyst) complex. This deactivates the nucleus to further substitution or any subsequent electrophilic acylation so that mono-acyl derivatives are easily isolable, and rearrangements with the acyl or the nuclear substituted products do not normally occur. This reaction is quite successful for many types of substrate, including fused ring systems. Compounds containing ortho/para-directing groups, including alkoxy, hydroxy, acetamido, and halogens, are easily acylated giving mainly or exclusively the para products because of the relatively large size of the acyl group²⁸.

II.1.1 Synthesis of 1,4-bis(4'-fluoro-1'-naphthoyl)benzene [I-1]

Ohno et al²⁹ carried out a Friedel-Crafts acylation reaction of 2,6-dimethylnaphthalene with 4-fluorobenzoyl chloride in the presence of aluminum chloride in nitrobenzene. The reaction was worked up by washing in 10% aqueous acid followed by washings in methanol. The reaction afforded 1,5-bis(4'-fluorobenzoyl)-2,6-dimethylnaphthalene in excellent yield.

The synthesis of [I-1] was attempted using a 2.6:1 molar ratio of aluminum chloride to terephthaloyl dichloride in nitrobenzene. During the course of the reaction, a bright red viscous solution resulted, arguably indicating the formation of the acylium ion. TLC (10% EtOAc/hexane as an eluent) showed the consumption of the starting material. Following the work-up in acid and methanol washings, recrystallization three times in

DMF afforded a yellow crystalline solid in good yield. The melting point was recorded as 228-229 °C; no literature value could be found. The DSC would indicate the purity of the compound as an HPLC could not be performed due to a solubility problem in the eluent for the HPLC. Moreover, although only slightly soluble in chloroform, ^1H and ^{13}C NMR (Figure II.2 and II.3) were obtained; the assignments of the ^1H and ^{13}C NMR chemical shifts are summarized in Tables II.1 and II.2 respectively. These assignments were supported by COSY and HETCOR experiments.

Figure II.2 ^1H NMR spectrum of 1,4-bis(4'-fluoro-1'-naphthoyl)benzene

Figure II.3 ^{13}C NMR spectrum of 1,4-bis(4'-fluoro-1'-naphthoyl)benzene

Table II.1: Summary of ^1H NMR data for 1,4-bis(4'-fluoro-1'-naphthoyl)benzene

^1H NMR	H_2	H_3	H_4	H_7	H_8	H_9	H_{12}
δ	7.62	7.19	8.22	7.66	7.84	8.32	7.92
J,Hz	m	8.0(3-2) 1.8(3-F)	m	m	m	m	-

Table II.2: Summary of ^{13}C NMR data for 1,4-bis(4'-fluoro-1'-naphthoyl)benzene

^{13}C NMR	C1	C2	C3	C5	C6	C7	C8
δ	162.0	129.8	107.9	141.7	120.8	126.8	128.5
J,Hz	-	10	21	-	6	-	-
^{13}C NMR	C9	C10	C11	C12			
δ	125.4	159.4	195.9	129.9			
J,Hz	2	-	-	-			

The complicated splitting patterns in the ^1H NMR, though already accounted for by the additional splitting due to the fluorine atoms, may also be a result of the possibility of isomers formed during the acylation reaction. It has been discovered³⁰ that rearrangement products as well as other isomers resulting from the Friedel-Crafts acylation reaction of 1-chloro and 1-fluoronaphthalenes occur in no more than very minor amounts. Moreover, fluoronaphthalene gives exclusively para-products. This is somewhat surprising since halides, like meta-directing groups, are known to deactivate an aromatic ring and might likewise be expected to lend to some heteronuclear electrophilic substitution in the naphthalene ring. Nonetheless, ^{19}F NMR data support

these findings as there was only one peak in the NMR at -114.811 ppm, relative to CCl_3F , indicating the presence of only one acylation product.

The IR spectrum showed a strong peak at 1651 cm^{-1} indicating the conjugated carbonyl moiety. MS shows the parent molecular ion at m/e 422 as expected and the base peak at m/e 173 corresponding to the loss of fluoronaphthoyl radical. The other fragmentations show patterns indicative of the structure. HRMS indicated the correct molecular formula.

The presence of the coupling in the naphthyl ring, the C-F coupling and high shift quaternary carbon in the ^{13}C NMR, the fragmentation patterns in the MS coupled with the HRMS, and the results of the ^{19}F NMR, clearly prove the structure of the 1,4-bis(4'-fluoronaphthoyl)benzene monomer [I-1].

Thus, this double Friedel-Crafts process yielded 1,4-bis(4'-fluoronaphthoyl)benzene in fairly high yield and in high purity. With the highly pure monomer at hand, polymerization may now be carried out.

II.1.2 Synthesis of 4-chloro-1-acetonaphthone

A Friedel-Crafts acylation was carried out with a 1.2:1 molar ratio of chloronaphthalene to acetyl chloride. Aluminum chloride was then added in a 1.3:1 molar ratio to the acetyl chloride at ice bath temperatures over a 30 minute period. The reaction mixture changed from clear/colorless to a reddish orange. After one hour, the temperature was raised to ca. $40\text{ }^\circ\text{C}$ and held for two hours. TLC (EtOAc/hexane as the eluent) showed the consumption of the starting materials so the ensuing reaction mixture was poured into ice-cold aqueous acid. The reaction mixture was extracted in chloroform, a 10% solution of sodium hydroxide, and fresh water. The mixture was then concentrated and distilled twice.

The IR indicated the aliphatic as well as olefinic C-H stretches at 3000 cm^{-1} and a carbonyl stretch at 1681 cm^{-1} . The ^1H NMR (Figure II.4) indicated the presence of the

Figure II.4. ^1H NMR spectrum of 4-chloro-1-acetonaphthone

methyl moiety at 2.75 ppm and the characteristic pattern of the naphthylene system in the aromatic region; however, some complicated splitting of the aromatic region was observed which could be the result of the possible 1,2-isomer also being present. After purification, the acid chloride was deemed sufficiently pure³⁰ to be used in the following step.

II.1.3 Synthesis of 4-chloro-1-naphthoic acid

4-chloro-1-naphthoic acid was obtained by hypochlorite oxidation of 4-chloro-1-aceto naphthone at 70-80 °C for three hours. TLC (10% acetone in hexane as the eluent) showed the reaction to be complete. The reaction mixture was quenched with sodium bisulfite and acidified with several drops of concentrated hydrochloric acid³⁰. The white precipitate was dissolved in an aqueous solution of 10% sodium hydroxide to remove any starting materials, was reacidified with conc. HCl, and finally recrystallized in ethanol affording a good yield of white crystals.

The melting point (221-222 °C) was in good agreement with the literature³⁰ value of 223-224 °C. The ¹H NMR spectrum (Figure II.5) of 4-chloro-1-naphthoic acid shows the disappearance of the methyl moiety at 2.75 ppm of the naphthone precursor.

The IR showed the most marked change in going from the naphthone to the acid (Figure II.6). There is an enormous change in the aliphatic stretch region (2900-3000 cm⁻¹), indicative to the formation of the acid; along with the change in the carbonyl region, going from 1681 cm⁻¹ for the ketone to 1698 cm⁻¹ for the acid.

The formation of 4-chloro-1-naphthoic acid was therefore confirmed from the above characterizations, and was used in the following reaction.

II.1.4 Synthesis of 4-chloro-1-naphthoyl chloride

The transformation of 4-chloro-1-naphthoic acid to the acid chloride was done using 4 fold excess of thionyl chloride. Generally, only a slight excess of thionyl

Figure II.5. ^1H NMR spectrum of 4-chloro-1-naphthoic acid

Figure II.6. Comparative IR Spectra of 4-chloro-1-aceto naphthone (A) and 4-chloro-1-naphthoic acid (B)

chloride are required, however this was not enough for the dissolution of the acid so a slight excess was added. The system was refluxed for 18 hours at ca. 80 °C. The excess thionyl chloride was distilled off (water aspirator) and the resulting brownish solid boiled in hexane. The product was vacuum distilled (1 mm Hg) for further purification affording a good yield of 4-chloro-1-naphthoyl chloride.

The IR showed the disappearance of the hydroxyl and the distinct shift in the carbonyl moiety from the carboxylic acid (1698 cm^{-1}) to that of the acid chloride (1752 cm^{-1}).

II.1.5 Synthesis of 4-chloro-1-(4'-fluoro-1'-naphthoyl) naphthalene [I-2]

A Friedel-Crafts reaction was carried out with a 3:1 molar ratio of fluoronaphthalene to acid chloride and a 1.4:1 molar ratio of Lewis acid to acid chloride in nitrobenzene. The reaction was carried out at ca. 70-80 °C and was stopped after 12 hours as TLC (10% acetone/hexane as eluent) showed the consumption of the starting material. The mixture was poured into ice cold aqueous HCl and worked up in methanol. The precipitate was vacuum distilled twice (1 mm Hg) and recrystallized in xylenes affording a good yield of yellow crystals.

The melting point was recorded to be 111-112 °C; no literature value was found. ^1H and ^{13}C NMR were run on the sample and are illustrated in figures II.7 and II.8 respectively. The spectra, though very complicated due to splitting and poor separation of peaks, were resolved with the use of lanthanide shift reagent - $[\text{Eu}(\text{fod})_3]$ and are summarized in tables II.3 and II.4.

Figure II.7. ^1H NMR spectrum of 4-chloro-1-(4'-fluoro-1'-naphthoyl)naphthalene [I-2] with 11 mg $[\text{Eu}(\text{fod})_3]$

Figure II.8. ^{13}C NMR spectrum of 4-chloro-1-(4'-fluoro-1'-naphthoyl)naphthalene [I-2] with 11 mg $[\text{Eu}(\text{fod})_3]$

Table II.3 Summary of ^1H NMR of 4-chloro-1-(4'-fluoro-1'-naphthoyl)naphthalene

^1H NMR	H_2	H_3	H_4	H_7	H_8	H_9
δ	7.62	7.65	9.06	7.62	7.70	8.46
J, Hz	m	7.6(3-2)	8.4(6-7)	m	m	8.4(9-8)
^1H NMR	H_{12}	H_{13}	H_{16}	H_{17}	H_{18}	H_{19}
δ	7.19	8.01	9.40	7.71	7.63	7.52
J, Hz	8.4(12-13) 1.2(12-F)	8.4(13-12) 1.3(13-F)	4.8(16-17)	m	m	m

Table II.4 Summary of ^{13}C NMR of 4-chloro-1-(4'-fluoro-1'-naphthoyl)naphthalene

^{13}C NMR	C1	C2	C3	C4	C5	C6	C7
δ	-	125.1	130.0	133.0	132.0	126.8	128.0
J, Hz	-	-	-	-	-	-	-
^{13}C NMR	C8	C9	C10	C11	C12	C13	C14
δ	127.1	125.0	131.0	124.0	108.0	133.2	133.8
J, Hz	-	-	-	15	20	8	-
^{13}C NMR	C15	C16	C17	C18	C19	C20	C21
δ	136.0	126.5	127.8	129.0	121.0	137.0	197.6
J, Hz	-	-	-	-	6	-	-

Lanthanide shift experiments were conducted with the NMR samples in aliquots of 0 mg to 11 mg of shift reagent, added in 2-2.5 mg aliquots. These experiments greatly enhanced the spectral resolution and coupled with COSY and HETCOR experiments, allowed for a more positive structural identification.

The IR gave indication to the conjugated carbonyl moiety at 1645 cm^{-1} as well as C-X stretches at 1243 and 758 cm^{-1} , indicating the respective carbon-fluorine and carbon-chlorine stretches. MS gave rise to the parent molecular ion at m/z 334 which was expected and the base peak at m/e 173 corresponding to the loss of the fluoronaphthoyl radical. The rest of the fragmentation patterns were indicative of the structure. Moreover, HRMS eluted to the correct molecular formula.

Although the splitting in the ^1H NMR is quite complicated due to the fluorine present, there still remains the possibility of isomers. However, the findings of Jacobs et al.³⁰ have shown that Friedel-Crafts acylation reaction with fluoronaphthalene gave *exclusively* *para* products. The ^{19}F NMR results again, supported these findings as only one peak showed up in the NMR at -114.146 ppm relative to CCl_3F .

Therefore, in reference to the above characterizations, the synthesis of 4-chloro-1-(4'-fluoro-1'-naphthoyl)naphthalene [I-2] was successful and polymerization can now be carried out.

Table II.5. Solubilities For [I-1] and [I-2]

Solvent	1,4-bis(4'-fluoronaphthoyl) benzene [I-1]		4-chloro-1-(4'-fluoronaphthoyl) naphthalene [I-2]	
	Cold	Hot	Cold	Hot
TCE	i	s	s	N/A
CHCl_3	i	ss	s	N/A
NMP	i	vs	s	N/A
DMF	i	vs(*)	s	N/A
DMAc	i	s(*)	s	N/A
NMC	i	s	ss	s
Cl-naph	i	s	s	N/A
1,2-dichloro- benzene	i	s	s	N/A
DMSO	i	s	ss	s

KEY: vs = very soluble; s = soluble; ss = slightly soluble; i = insoluble; N/A = not applicable; (*) = crystallizes out on cooling.

Monomer [I-1] is insoluble at room temperature as opposed to monomer [I-2], which is soluble or slightly soluble at room temperature. This can be attributed to the

orientation of the naphthalene moieties. The [1-1] monomer is probably aligned in a coplanar fashion which would allow for tighter packing of molecules and less solvent interaction. The [1-2] monomer, because of steric hindrance between the naphthalene units, probably has the naphthalenes in a periplanar-type orientation, thus allowing for looser packing and consequently, greater solvent interaction.

CHAPTER III. Synthesis of Naphthalene-based Poly(arylene ether Ketone)s

III.1. Polymerization Reaction.

Different reaction parameters were utilized for the optimization of the polymer molecular weight including solvents and reaction temperatures. In general, NMP, DMAc, and TMSO_2 are common solvents for nucleophilic substitution polycondensations. When the polymerizations were carried out in NMP at 160 °C with toluene as an azeotroping agent, only low molecular weight polymers were obtained presumably because of the chain cleavage by potassium fluoride⁶. In both DMAc and NMP, polymers exhibited solubility problems. Therefore, polymerizations would have to be carried out under slightly harsher conditions (i.e., higher reaction temperatures). This solution, however, may bring about yet another complication as it has been reported³¹ that fluoride ion can cleave the ether bond at elevated temperatures. Nonetheless, the polymerizations were carried out in TMSO_2 with chlorobenzene as an azeotroping agent at 210 °C yielding moderately high molecular weight polymers (η_{inh} ranging from 0.3-0.6 dL/g).

Polymerizations were performed using a stoichiometric ratio of monomers in the presence of excess (2 equiv.) of K_2CO_3 in TMSO_2 at ca. 25% solid content (Scheme III.1.) The reaction temperature was gradually raised to 210 °C, with any water formed during the reaction removed as an azeotrope with the chlorobenzene at ca. 140 °C, and maintained for 2-6 hours. During the course of the reaction, the reaction mixture became increasingly viscous and was analyzed by gel permeation chromatography to obtain the molecular weight distributions.

Scheme III.1. Synthesis of Poly(arylene ether ketone)s

The reaction was stopped when the molecular weight (as per GPC) and the viscosity began to fall. The resulting polymers were coagulated in an excess of methanol, followed by reverse precipitation to remove any remaining oligomers.

Under these reaction conditions, four of the above polymers (III-1c,d & III-2c,d) displayed solubility problems and precipitated out of solution prematurely resulting in low molecular weight polymers. One obvious solution to this problem was to use DPS as a reaction "melt" medium as this was used in the preparation of the well-known PEEK^{4,32}. Inherent difficulties with this approach, however, are first, the cost of DPS, and second, the sublimation of the DPS at elevated temperatures (>300 °C). These harsh conditions could also bring upon the problem of possible ether cleavage as was previously mentioned. The polymerization was performed using [I-2] and Hydroquinone in stoichiometric ratios with an excess of K₂CO₃ and DPS in ca. 25% solid content. Because of the high reaction

temperatures (300 °C), and as water and DPS are not miscible, no azeotoping agent was needed. As the polymer turned out to be insoluble in CHCl_3 , GPC monitoring of the molecular weight during the reaction was not possible. Therefore, the solution viscosity was the only indication of the growing molecular weight and as it visibly diminished, the reaction was stopped. The polymer was poured onto a metal plate where solidification was immediate, crushed, and finally boiled in CHCl_3 for 30 minutes for the removal of any soluble products. The polymer was dried in a vacuum oven at 150 °C for 12 hours.

Because of the difficulties in using DPS, somewhat milder conditions were sought. Two higher boiling solvents (higher than TMSO_2) were tried: 1-cyclohexyl-2-pyrrolidinone (bp: 280 °C @ 1 atm) and N-methylcaprolactam (bp: 260 °C @ 1 atm). With the former, the system was brought to 210 °C and held for several hours, azeotrope off water with chlorobenzene at ca. 140 °C. The temperature was then raised to 280 °C and maintained for 2 hours. The dark solution (presumably burnt or decomposed³¹) was refluxed in hexane and set aside for further analysis if needed. Serendipitously, the latter solvent was found to keep low molecular weight polymers III-1c,d and III-2c,d in solution at temperatures as low as 200 °C. Polymerizations were again carried out in stoichiometric amounts of monomer in the presence of excess (2 equiv.) of K_2CO_3 in NMC at ca. 25% solid content.

III.2. Characterization and Properties

Polymers III-1a,b,e and III-2a,b,e were off-white to creamy yellow fibrous solids that displayed excellent solubility in chlorinated hydrocarbons, DMAc, and NMP. Polymers III-1c,d and III-2c,d were off-white granular solids whose solubilities in chlorinated and other solvents are outlined in Tables III.1 and III.2 respectively.

Table III.1. Solubility of Polymers III-1c and III-2c

Solvent	Polymer III-1c		Polymer III-2c	
	Cold	Hot	Cold	Hot
TCE	i	s	i	ss
CHCl ₃	i	i	i	i
NMP	s	N/A	s	N/A
DMF	i	i	i	i
DMAc	i	ss	i	i
NMC	s	N/A	i	s
Cl-naph	i	s	ss	s
DMSO	ss	ss	ss	ss

KEY: s = soluble; ss = slightly soluble; i = insoluble; N/A = not applicable

Table III.2. Solubility of Polymers III-1d and III-2d

Solvent	Polymer III-1d		Polymer III-2d	
	Cold	Hot	Cold	Hot
TCE	i	s	i	ss
CHCl ₃	i	i	i	i
NMP	s	N/A	s	N/A
DMF	i	i	i	i
DMAc	i	ss	i	i
NMC	s	N/A	i	s
Cl-naph	i	s	ss	s
DMSO	ss	ss	ss	ss

KEY: s = soluble; ss = slightly soluble; i = insoluble; N/A = not applicable

Polymers III-1a,b and III-2a,b contain flexible aliphatic carbon centers that enabled the polymer backbone ample room for rotational freedom which accounted for the solubilities in hot and cold solvents. The large fluorene group (polymers III-1c and III-2c), because of its spiro-cardo structure, showed good solubility². Polymers III-1c,d and III-2c,d, on the other hand, displayed much more solvent resistance than the others. The more linear portions of the backbone provide for much more restriction to motion and allow

for much tighter packing of the polymers which would account for the increased solvent resistance.

III.2.1. Spectroscopic Characterization

The ^1H NMR spectrum of polymers III-1a,b,e and III-2a,b,e showed the same characteristic pattern of the naphthalene units as did the monomers [I-1] and [I-2]. The results of the ^1H and ^{13}C NMR for polymer III-2a are illustrated in Figures III.1. and III.2. and are further reported in tables III.3 and III.4 respectively. The assignments were supported by COSY and HETCOR experiments.

Table III.3. ^1H NMR Results of Polymer III-2a

^1H NMR	H_3	H_4	H_7	H_8	H_9	H_{10}	H_{13}	H_{14}	H_{17}
δ	7.45	6.65	8.38	7.54	7.56	8.60	7.21	6.98	1.65
J, Hz	8.1	8.0	8.1	m	m	8.2	8.6	8.6	s
	(3-4)	(4-3)	(9-8)			(6-7)	(13-14)	(14-13)	

Table III.4. ^{13}C NMR Results of Polymer III-2a

^{13}C NMR	C1	C2	C3	C4	C5	C6
δ	198	157	131	109	154	132
^{13}C NMR	C7	C8	C9	C10	C11	C12
δ	122	127	129	126	133	146
^{13}C NMR	C13	C14	C16	C17		
δ	128	119	42	31		

The ^{13}C NMR spectrum of III-2a showed 17 distinguishable peaks for each of the representative carbon atoms. The spectrum cannot be directly compared with that of the starting monomer as the monomer [I-2] is unsymmetrical due to the two halides present and consequently has double the number of lines. Furthermore, there is additional splitting due to the fluorine. Upon polymerization and consequent displacement of the halides, symmetry in the monomer portion was acquired making for a much simpler spectrum, with additional and easily identifiable carbons from the bisphenoxy portion.

The IR indicated the carbonyl moieties absorbing for these polymers in the region of $1648\text{-}1658\text{ cm}^{-1}$ with the etheral linkages being confirmed by strong absorptions in the region $1238\text{-}1243\text{ cm}^{-1}$. These spectral data clearly indicated the formation of the expected polymers.

Figure III.1. ^1H NMR spectrum of Polymer III-2a

Figure III.2. ^{13}C NMR spectrum of Polymer III-2a

As can be seen in Tables III.1 and III.2, polymers III-1c,d and III-2c,d exhibited good solvent resistance and as a result of this, coupled with the availability of deuterated solvents for NMR, NMRs were not obtained for these polymers. Internal reference-type methods using NMC to solvate the sample with acetone- d_6 as the internal reference were attempted but to no avail. The spectra were folded back and there was barely, if at all, any spectral resolution whatsoever. Therefore, the only structural proof of these polymers via spectroscopic methods would be by that of IR, which, only indicates the functionalities present.

The IR indicated carbonyl absorptions in the range of $1641\text{--}1654\text{ cm}^{-1}$ and strong etheral linkages in the area of $1221\text{--}1232\text{ cm}^{-1}$. Given the previous success for the other 6 polymers prepared under similar polymerization conditions and with reference to the carbonyl and ether moieties being present in the same region as for the other polymers, the successful formation of the polymers can be expected.

III.2.2. Molecular Weight

The molecular weight of a polymer is of prime importance in its synthesis and application. Important aspects such as thermal and mechanical properties are all dependent on the molecular weight. In general, the physical attributes of the polymer increase with increasing molecular weight until a limit is reached at which point, changes in the molecular weight affect those properties in a limited fashion. The attainment of high molecular weight is dependent upon the accurate control of stoichiometry ie. the molar ratio of reactants (which may also include the base) undergoing polycondensation. The minimum useful molecular weight, usually in the range of $5,000\text{--}10,000\text{ g/mol}$, differs for different polymers³³.

In order to obtain the molecular weight distributions of the polymers during the course of the reaction, gel permeation chromatography (GPC) was used. All GPC traces were monomodal with polydispersity factors (M_w/M_n) ranging from 1.36 to 2.20. The

polymers exhibited Gaussian distributions with a smaller low molecular weight peak, presumably due to small amounts of oligomers still present. A typical example is shown in Figure III.3.

For polymers III-1a,b,e and III-2a,b,e, GPC in chloroform relative to polystyrene showed that relatively low to moderately high molecular weight products were obtained (Table III.5). The apparent weight average molecular weight for these polymers ranged from 38,000 to 84,000 g/mol. The inability to obtain a high molecular weight from polymer III-2e (38,000 g/mol) was quite surprising since the monomer was of high purity as indicated by the sharp melting peak (DSC), coupled with NMR spectroscopy, as well as MS and HRMS⁵. High molecular weight polymers (phenyl analogues) have been reported⁵ using essentially the same reaction conditions. This difference may be attributed to any one of several factors, such as heating rate, final reaction temperature and time, and particle size and quantity of potassium carbonate used. However, the fact of the naphthylene being larger than benzene, first comes to mind, which would bring about solubility problems in the preparative stages which in turn could lead to low molecular weight polymers.

In comparison to the high molecular weight (83,223 g/mol) obtained for its diketone counterpart (III-1e), the "CO-ph-CO" in the monomer allows for freer rotation about the polymer backbone and consequently, less steric hindrance between the naphthalene rings leading to better solubility. Thus, the stoichiometry of the reactants is affected and a polymer of low molecular weight is obtained.

Other methods used in determining the average molecular weight of polymers are based on solution properties. These would include methods based on light scattering, and viscosity^{34,35}. The various methods do not yield the same average molecular weights as the properties being measured are biased differently towards the different-shaped polymer molecules in a polymer sample.

Assuming that similar structures are being compared, higher viscosities correspond to higher molecular weights. Both inherent and intrinsic viscosities were run on the polymers giving results from 0.21 to 0.66 dL/g. in chloroform and NMC (Table III.5).

Along with viscosity measurements, the molecular weight for a polymer can be said to be high if flexible films can be prepared. The molecular weight can be approximated by the preparation and film integrity (flex). Films in chloroform were successfully prepared for polymers III-1a,b,e and III-2a,b,e but not for polymers III-1c,d and III-2c,d.

Although film integrity is influenced by crystallinity (more crystalline, the more brittle the film), films for polymers III-1c,d and III-2c,d were not made with any degree of success.

**Table III.5. Molecular Weight, Inherent and Intrinsic Viscosities for
Polymers III-1a-e and III-2a-e**

Polymer		Mw ($\times 10^{-4}$)	Mn ($\times 10^{-4}$)	Mw/Mn	η_{inh}^a (dL/g)	η_{int}^a (dL/g)
III-1	a	5.71	2.74	2.08	0.34	0.30
	b	8.39	3.81	2.20	0.29	0.48
	c	N/A	N/A	N/A	0.33 ^b	0.40 ^b
	c ^c	N/A	N/A	N/A	0.23 ^b	0.21 ^b
	d	N/A	N/A	N/A	0.34 ^b	0.30 ^b
	e	8.32	6.12	1.36	0.66	0.51
III-2	a	5.71	2.13	1.58	0.24	0.21
	b	5.81	3.67	1.58	0.44	0.47
	c	N/A	N/A	N/A	0.31 ^b	0.22 ^b
	d	N/A	N/A	N/A	0.31 ^b	0.31 ^b
	e	3.80	2.13	1.78	0.23	0.21

^a measured in 0.5% chloroform at 25 °C; ^b measured in 0.5% NMC at 25 °C; ^c polymerized in DPS; N/A = not available

Figure III.3. GPC Traces For Polymer III-1a

III.2.3. Thermal Properties

Polymeric materials are characterized by two major types of transition temperatures, the crystalline melting temperature (T_m) and the glass transition temperature (T_g).

None of the polymers prepared in TMSO_2 or NMC showed any crystalline behavior as assessed by DSC. The T_g s obtained ranged from 204 to 274 °C depending on the units derived from bisphenol monomers (Table III.6). Polymer III-1c, when prepared from DPS, exhibited crystalline behavior as was indicated by DSC (Figure III.4.). The DSC trace showed both a T_g and a T_m suggesting a semicrystalline nature.

Figure III.4. DSC Trace of Semicrystalline Polymer III-1c

Semicrystalline polymers exhibit enhanced physical and mechanical properties with respect to their amorphous counterparts. This phenomenon was observed as the T_g and thermal decomposition (in N_2) of polymer III-1c prepared in DPS versus III-1c prepared from NMC (Table III.6).

Table III.6. DSC and TG Results for Polymers III-1a-e and III-2a-e

Polymer		T _g ^a (°C)	T _d ^b (N ₂)	T _d ^b (static air)
III-1	a	204	492	436
	b	210	562	511
	c	209	493	489
	c ^c	217	504	474
		310 ^d		
	d	230	480	430
	e	265	526	464
III-2	a	212	497	478
	b	233	519	528
	c	232	510	524
	d	235	488	466
	e	273	525	453

^a second scan at heating rate of 10 °C/min; ^b Temperature for 5% weight loss; ^c Prepared in DPS; ^d Crystalline Melting Point.

An overview of polymers III-1a-e and III-2a-e indicates that all the reported Tgs are moderately high. The rigidity of polymers increases when there are aromatic structures in the main polymer backbone². Polymers III-2a-e displayed greater thermal properties (Tgs) than their III-1a-e structural counterparts. This was expected since the diketone series contains two carbonyls separated by a phenyl ring which allows for more bond rotation and consequently, lower Tg values. In looking at either series, bulky cardo groups such as fluorene groups in the polymer backbone leads to significant increases in Tg while providing good solubility⁵. Polymers III-1e and III-2e gave Tgs of 265 and 273 °C respectively which were considerably higher than the Tgs found for the other polymers.

As expected, the polymers with the lowest Tgs were those prepared from BPA (III-1a and III-2a) and 4,4'-(hexafluoroisopropylidene)diphenol (III-1b and III-2b). These bisphenols contain no bulky groups but a flexible propylidene group. Moderate Tgs were obtained from polymers prepared from 1,4-hydroquinone (III-1c and III-2c) and 4,4-diphenol (III-1d and III-2d) which are rigid but not bulky.

Because of the inherent crystallinity of polymer III-1c prepared in DPS, it was thought that polymers III-1c,d and III-2c,d may be crystalline or at least have crystallinity induced. As the extent of crystallinity can be significantly increased in polymers via mechanical stretching to align and crystallize the polymer chains, or by thermal annealing, the four polymers were annealed to temperatures 20-30 °C above the Tg but below Tm in an attempt to crystallize the samples, as well as 20-30 °C above the Tm in an attempt to obtain the crystallization temperature (Tc). Temperatures were held for varying times before cooling in liquid nitrogen or ice water. The DSC traces showed slight increases in Tg but no signs of any Tm. WAXS analysis showed no appreciable degree of crystallinity for these polymers produced in NMC. Structurally related polymers are illustrated below.

Figure III.5. DSC Traces for Polymers III-1c,d and III-2c,d

Figure III.6. Structurally Related Analogues ¹³

As can be seen (Table III.6), the dinaphthyl containing polymers exhibit higher Tgs and Tms than their phenyl analogues containing hydroquinone and diphenol (Figure III.6.). Polymers III-1c,d and III-2c,d display even higher Tgs, as is expected but no crystallinity as the twisted confirmation of the bulky naphthalene rings prevents effective crystallization giving way to amorphous polymers. In reference to the semicrystalline polymer III-1c (prepared in DPS), crystallization is observed but with a lower Tm as a result of the bulky nature of the naphthalene.

The thermooxidative stabilities of the polymers were measured by thermogravimetric analysis (TG) in nitrogen and static air (Table III.6.). Polymers III-1a-e indicated a 5% weight loss in nitrogen ranging from 480 to 562 °C and 430 to 511 °C in static air. Polymers III-2a-e indicated a 5% weight loss in nitrogen ranging from 488 to 525 °C and 453 to 528 °C in air. As can be seen in Table III.6., polymer decomposition occurs more rapidly, in most cases, in static air than in nitrogen.

Figure III.7. Thermograms of Polymer III-1a-e

III.4. Mechanical Properties

Many polymer properties such as solvent, electrical resistance, and gas permeability are important in determining the specific use of a polymer in a specific application. However, the prime consideration in determining the general utility of a polymer is its mechanical behavior, that is, its deformation and flow characteristics under stress. The mechanical behavior of a polymer can be characterized by its stress-strain properties³⁶.

The Young's moduli (E') of polymers III-1b,e and III-2a,b,e were obtained from thermomechanical analysis (TMA) in the tensile stress-strain mode (Table III.7). The measurements were performed on thin strips of films prepared from chloroform that were dried in a vacuum oven for several days. All films were tough, flexible, and transparent. A brittle, opaque deposit resulted when casting was attempted with polymer III-1a and was therefore unusable. Moreover, due to the solubility problems for polymers III-1c,d and III-2c,d, another solvent system (chloronaphthalene) was attempted for casting but this did not work.

Young's modulus gives an indication of the stiffness of the materials. In both series of polymers (Table III.7.) E' is approximately twice as great for the BPA/6FBPA-containing polymers than for the fluorene-containing ones. Phenyl-containing analogues (Figure III.6.) with the fluorene bisphenol have shown the opposite effect³⁷. This observation must be due to the bulkiness of the naphthalene moieties in the preparative stages of the polymers resulting in lower molecular weight polymers. E' for III-1e is also twice as great as that of III-2e because of the molecular weight differences (Table III.5.) of the two polymers.

As the temperature increases, Young's modulus remains high until the T_g is reached at which point, the modulus drops sharply. Therefore, the T_g can also be obtained by TMA measurements, taken as the maximum value of the $\tan \delta$ peak (Table III.7.). When compared to the T_g values obtained by DSC (Table III.6), polymers III-1b,e and III-2e showed very little change. The drop shown by polymer III-2a (ca. 33 °C) could be

Table III.7. TMA Results for Polymers III-1b,e and III-2a,b,e

Polymer		Tg ^a (max. Tan δ)	E' ^b (GPa)
III-1	b	201	4.20
	e	249	2.84
	a	177	3.44
III-2	b	176	2.29
	e	265	1.20

^a Tan δ value, at a heating rate of 10 °C/min, ^b Young's modulus at 25 °C, load A: offset = 10 g., Amp = 5 g.

attributed to chloroform solvent remaining in the film or to low molecular weight. In either case, the value obtained for E' is unreliable.

The Young's moduli for the two series of polymers, when compared to elastomers (natural rubbers having E' in the order of 10⁶ Pa), are 3 orders of magnitude greater and consequently, fall in the range of those for poly(ether ketone)s .

CONTRIBUTION TO KNOWLEDGE

1. Monomers: [I-1] synthesized via a double Friedel-Crafts acylation of terephthaloyl dichloride with fluoronaphthalene.

[I-2] synthesized after the hypochlorite oxidation of the naphthone and the thionyl chloride substitution with the naphthoic acid, via Friedel-Crafts acylation. Both monomers were obtained in high yield after purification by recrystallization

2. Polymer synthesis: nucleophilic displacement of the monomers with a variety of bisphenols using potassium carbonate as a base and TMSO_2 and N-methyl caprolactam as solvents.

3. Polymer properties: Tgs, measured by differential scanning calorimetry, ranged from 204 to 273 °C. The 5% weight loss of the polymers by thermogravimetry occurred all above 480 °C in nitrogen and 430 °C in static air. Thermochemical analysis showed good resistance of the polymers to tensile stress. Young's moduli for the polymers ranged from 1.20 to 4.20 GPa.

EXPERIMENTAL SECTION

GENERAL METHODS.

Aluminum chloride, fluoboric acid (48% wt solution in water), tetramethylene sulfone (TMSO₂), potassium carbonate, acetyl chloride, sodium hypochlorite (NaOCl), sodium nitrite (NaNO₂), terephthaloyl dichloride, isophthaloyl dichloride, thionyl chloride (SOCl₂), N-methyl-2-pyrrolidinone (NMP), and other common organic solvents were purchased from Aldrich Chemical Co. and used as received. N,N-dimethylacetamide (DMAc) (Aldrich) was distilled over P₂O₅. Chloronaphthalene was fractionally distilled under vacuum (water aspirator). 1-Amino-naphthalene was purchased from Fluka Chemical Corp. 4,4'-Isopropylidenediphenol (III-a, BPA) (Aldrich), 4,4'-hexafluoroisopropylidenediphenol (III-b) (Aldrich), 4,4'-bisphenol (III-c) (Aldrich) 1,4-hydroquinone (III-d) (Aldrich), and 9,9 bis-(4-hydroxyphenyl) fluorene (III-e) (General Electric Co.) were purified by recrystallization.

CHARACTERIZATION

Melting points were taken on the Fisher-Johns melting apparatus and are uncorrected. The ¹H and ¹³CNMR were recorded on either the Varian Gemini-200 or the Bruker-400 instrument using tetramethylsilane as the internal solvent. Infrared measurements were performed on the Perkin-Elmer Series 1600 FTIR instrument. Molecular weights were determined on a Perkin-Elmer LC-250 GPC instrument relative to Polystyrene standards using chloroform as an eluent at a flow rate of 2.0 mL/min; a UV detector was set at 254 nm wavelength. Inherent viscosities were measured in a 0.5 g/dL chloroform solution (N-methylcaprolactam where indicated) at 25 °C using an Ubbelohde dilution viscometer. Intrinsic viscosities were measured in concentrations of 0.5 g/dL, 0.33 g/dL, and 0.25 g/dL chloroform solutions (N-methylcaprolactam where indicated) at 25 °C on the same instrument. 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 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 and air (flow rate of 200 mL/min).

FILM CASTING

Polymer films were cast in either chloroform or N-methyl caprolactam. A typical procedure is as follows: a polymer (200 mg) is dissolved in 4 mL solvent. The solution is filtered and transferred to a glass ring (diameter = 3.0 cm, height = 2 cm, thickness = 0.2 cm) placed on a glass plate. The ring is covered and the solvent allowed to evaporate (slowly) over a 48 h period at room temperature. The resulting film is then dried under vacuum at $T = 100 - 300$ °C for 3-5 days. Film thickness ranged from 0.13 mm - 0.19 mm.

DSC EXPERIMENTS

Annealing and quenching experiments were performed on polymers III-1c,d and III-2c,d from the original DSC samples using 6-10 mg each of sample. Samples were heated at a rate of 50-60 °C/min to a temperature between the T_g and T_m as well as to a temperature 20-30 °C above T_m with holding times ranging from 5-60 min. Quenching was done both in liquid nitrogen and in ice water affording similar results. Immediately after quenching, a normal DSC scan was run showing a slight increase in T_g . No substantial T_c (crystallization temperature) was observed.

MEASUREMENT OF MECHANICAL PROPERTIES

A typical procedure for obtaining Young's modulus measurements is as follows: a film strip (length = 5 mm, width = 2 mm, thickness = 0.06 mm) cut from a stamp was mounted in a Seiko TMA/SS 120 instrument. For the Young's modulus at 25 °C, the parameters were set as follows: offset load = 10-20 g, load amplitude = 5-10 g, and cycling frequency = 0.05 Hz. A second of Young's modulus was then run on the same sample with identical load parameters at higher temperatures to obtain the Loss modulus (E'').

MONOMER SYNTHESIS

Fluoronaphthalene. A mixture of 1-naphthylamine (14.3 g; 0.1 mol) water (150 mL) and conc HCl (15 mL) was placed in a 1L erlenmeyer flask and gently heated with stirring until solvation was complete. An additional 20 mL conc. HCl was then added slowly and the resulting pink paste was cooled on ice with constant stirring. A solution of 8.0 g (0.12 mol) NaNO_2 in water was slowly added and the reaction mixture stirred vigorously for 15 - 20 min. Fluoboric acid (HBF_4 ; 48% wt sol.) was then added forming a tan coloured diazoniumborofluorate salt which was filtered, air dried, and finally dried in the oven at 50 °C for 1 h. The salt was placed in a 250 mL round bottom flask and heated with a bunsen burner just to the point of decomposition at which time the flame was removed and the cracking allowed to proceed on its own - thick whitish yellow gas (BF_3 and N_2) evolved. Once the reaction was over, the flame was reapplied to drive off any remaining fluoronaphthalene. The obtained product was transferred in a minimal amount of chloroform, washed with 5% NaOH, and distilled (at 85 °C under vac.- water aspirator) yielding 6.7 g (ca. 50%) fluoronaphthalene. The product was pure by HPLC, mp, etc.

4 Chloro-1-(4'-fluoro-1'-naphthoyl)naphthalene [I-2]. A 1L 3-neck round bottom flask equipped with a solid addition funnel and condensor was purged with nitrogen for 20 min. prior to use and flame dried. The vessel was charged with 1-chloronaphthalene (100.0 g; 0.615 mol), acetyl chloride (24.1 g; 0.301 mol), and dichloromethane (250 mL) forming a clear, colourless solution. Aluminum chloride (53.3 g; 0.400 mol) was added slowly at 0-5 °C (ice bath temperature) resulting in a deeply red coloured mixture. The reaction mixture became viscous so additional solvent was added (400 mL → 650 mL in total) and stirred at this temperature for 1 h and then raised to ca. 40 - 60 °C and maintained for 12 h. The reaction mixture was quantitatively transferred (CHCl_3) to an ice cold 10% HCl/water solution and stirred for 30 min. The dark coloured mixture was extracted in CHCl_3 , 5% aqueous NaOH, and finally fresh

water. The resulting emulsions were filtered, washed with CHCl_3 and added to the rest of the collections. The red solution was dried over MgSO_4 , filtered and evaporated yielding a crude oily residue, which was distilled under vacuum (water aspirator) yielding 53.5 g (0.262 mol) 4-chloro-1-acetonaphthone which was used in the following reaction.

To a 3L round-bottomed flask equipped with mechanical stirrer, 4-chloro-1-acetonaphthone, (52.1 g; 0.252 mol) NaOCl (1.2 L, 6.4 equiv.) and methanol (co-solvent: 10%) were added and stirred at 40 - 60 °C for 12 h. The once lime-green solution (now brown) was quenched with sodiumbisulfite (60 g in 300 mL water) turning the reaction mixture opaque white, and then acidified (100 mL conc HCl slowly) forming a fluffy white precipitate. The system was stirred for 2 h. The precipitate was dissolved in base (5% NaOH), filtered to remove any residual starting materials, and reacidified forming a white precipitate. This crude acid was filtered and recrystallized in abs. ethanol yielding 27.9 g (0.193 mol) 4-chloro-1-naphthoic acid and was used immediately in the following reaction.

A 1L round-bottomed flask was charged with 4-chloro-1-naphthoic acid (27.8 g; 0.135 mol) and SOCl_2 (1.5 equiv, 20 mL) however, this was not enough to solvate the acid so more SOCl_2 was added until solvation was complete and the system was stirred and refluxed at ca 80 °C for 12 h. The excess SOCl_2 was distilled off (water aspirator) leaving a light brown solid residue (IR indicated the disappearance of the hydroxyl [acid] and the distinct shift of the carbonyl moiety from the carboxylic acid [1698.2 cm^{-1}] to that of the acid chloride [1752.3 cm^{-1}]). The crude acid chloride was vacuum distilled (1 mmHg) yielding 28.3 g; (0.126 mol) 4-chloro-1-naphthoylchloride mp: 222-223 °C (lit. 223-224 °C) which was used in the following reaction.

A 100 mL 3-neck round-bottomed flask was flame dried, purged with N_2 and charged with 4-chloro-1-naphthoyl chloride (8.00 g; 35.6 mmol), fluoronaphthalene (15.3 g; 3 equiv.) and nitrobenzene (30 mL). The system was stirred until solvation was complete and while at a temperature of 0 - 5 °C (ice bath temp.) aluminum chloride (4.21

g; 1.40 equiv.) was added turning the solution a deep red colour. The system was maintained at this temperature for 1 h and was then gradually raised to ca 60 - 70 °C and allowed to continue for 8 h. The reaction mixture was poured quantitatively i. to an ice cold 10% HCl/water solution and stirred for 30 min resulting in an oily precipitate. The residue was then washed with 3 aliquots of methanol to remove any of the nitrobenzene solvent and then once with water, eventually leaving a solid residue. The crude binaphthyl ketone was filtered and recrystallized in abs. ethanol affording 6.21 g (18 mmol) 4-chloro-1-(4'-fluoro-naphthoyl) naphthalene [I-2] mp 111 - 112 °C, IR (KBr, cm⁻¹) 1645 (C=O), 1243.8 (C-F), 758.6 (C-Cl), ¹H NMR (400 MHz, Eu(fod)₃) 9.40 (d, 1H, J_{H-H} = 4.8 Hz), 9.06 (d, 1H, J_{H-H} = 8.6 Hz), 8.46 (d, d, 1H, J_{H-H} = 8.4 Hz, ⁴J_{H-H} = 0.8 Hz), 8.29 (m, 1H), 8.01 (m, 1H), 7.85 (d, 1H, J_{H-H} = 7.6 Hz), 7.68 (m, 5H), 7.19 (t, 1H, J_{H-H} = 8.4 Hz), ¹³C NMR (100 MHz) 198.99, 163.06, 160.47, 137.60, 136.58, 133.20, 132.96, 131.34, 130.12, 129.41, 128.67, 127.81, 127.19, 126.80, 126.59, 125.11, 125.09, 124.36, 121.17, ¹⁹F NMR (300 MHz, DMSO) -114.145 (s, 1F), MS (m/e) 334 (M⁺), 299 (M⁺ - Cl), 189 (M⁺ - Fnaph), 173 (M⁺ - Clnaph), 161 (M⁺ - COnaphF), 145 (M⁺ - COnaphCl), 126 (M⁺ - ClCOnaphF).

4-Chloro-1-(4'-chloro-1'-naphthoyl)naphthalene was prepared, as described for the synthesis of [I-2], from 4-chloro-1-naphthoyl)naphthalene and chloronaphthalene in nitrobenzene. The product was recrystallized from abs. ethanol yielding 11.5 g (34.4 mmol) 4-Chloro-(4'-chloronaphthoyl)naphthalene mp:131-132 °C, ¹H NMR (400 MHz, Eu(fod)₃) 8.86 (d, 1H, J_{H-H} = 8.2 Hz), 8.42 (d, d, 1H, J_{H-H} = 8.2 Hz, ⁴J_{H-H} = 1.3 Hz), 7.70 (d, 1H J_{H-H} = 7.7), 7.66 (t, d, 1H, J_{H-H} = 5.9 Hz, ⁴J_{H-H} = 1.4 Hz), 7.64 (t, d, 1H, J_{H-H} = 6.9 Hz, ⁴J_{H-H} = 1.5 Hz), ¹³C NMR (100 MHz, Eu(fod)₃) 197.88, 138.82, 136.63, 132.09, 130.96, 129.99, 128.57, 127.63, 126.08, 124.81, 124.72, MS (m/e) 350 (M⁺), 315 (M⁺ - Cl), 280 (M⁺ - 2Cl), 189 (M⁺ - Clnaph), 161 (M⁺ - COnaphCl), 126 (M⁺ - ClCOnaphCl).

1,4 -bis(4'-fluoro-1'-naphthoyl)benzene [I-1]. A 500 mL 3-neck round-bottomed flask was equipped with a solid addition funnel, condensor, and was purged with nitrogen for 20 min. prior to use. The reaction vessel was charged with terephthaloyl dichloride (12.6 g; 62.1 mmol), fluoronaphthalene (22.8 g; 0.155 mol; 2.5 equiv.) and nitrobenzene (100 mL), and once solvation was complete, aluminum chloride (21.5 g; 0.161 mol; 2.6 equiv.) was added to the yellow mixture in portions at 0 - 5 °C (ice bath temp.) and stirred for 1 h. The now red reaction mixture became too viscous for stirring so an additional 60 mL solvent was added → (160 mL total) and the temperature raised to ca. 60 - 80 °C for 3 h. The reaction mixture was worked up as for 4-Chloro-1-(4'-fluoro-naphthoyl)naphthalene [I-2] and was recrystallized in DMF 3x affording 17.0 g (40.2 mmol) dinaphthyl-diketone. mp: 230-231 °C, IR (KBr, cm^{-1}) 1651 (C=O), 1245 (C-F), ^1H NMR (400 MHz) 8.32 (m, 1H), 8.22 (m, 1H), 7.92 (s, 2H), 7.64 (m, 3H), 7.19 (t, 1H, $J_{\text{H-H}} = 8.0$ Hz), ^{13}C NMR (100 MHz) 195.94, 102.02, 159.44, 141.73, 131.22, 129.98, 129.75 ($J_{\text{C-F}} = 10$ Hz), 127.52, 126.85, 125.46 ($J_{\text{C-F}} = 2.0$ Hz), 120.79 ($J_{\text{C-F}} = 6.0$ Hz), 107.96 ($J_{\text{C-F}} = 21.0$ Hz), ^{19}F NMR (300 MHz, TCE) -114.811 (s, 2F), MS (m/e) 422 (M^+), 277 ($\text{M}^+ - \text{Fnaph}$), 249 ($\text{M}^+ - \text{CONaphF}$), 173 ($\text{M}^+ - \text{PhCONaphF}$), 145 ($\text{M}^+ - \text{FnaphCOPhCO}$).

1,4-bis(4'-chloro-1'-naphthoyl)benzene - was prepared as [I-1] using terephthaloyl dichloride and chloronaphthalene in nitrobenzene. The product was recrystallized in DMAc, yielding 2.71 g (5.96 mmol) 1,4-Bis(4'-chloronaphthoyl)benzene mp: 240-241 °C, IR (KBr, cm^{-1}) 1649 (C=O), ^1H NMR (400 MHz) 8.40 (d, 1H, $J_{\text{H-H}} = 8.4$ Hz), 8.18 (d, 1H, $J_{\text{H-H}} = 8.4$ Hz), 7.92 (s, 4H), 7.66 (d, t, 1H, $J_{\text{H-H}} = 8.4$ Hz, $^4J_{\text{H-H}} = 1.2$ Hz), 7.63 (d, 1H, $J_{\text{H-H}} = 7.6$ Hz), 7.61 (d, t, 1H, $J_{\text{H-H}} = 8.4$ Hz, $^4J_{\text{H-H}} = 1.2$ Hz), 7.51 (d, 1H, $J_{\text{H-H}} = 7.6$ Hz), MS (m/e) 454 (M^+), 419 ($\text{M}^+ - \text{Cl}$), 265 ($\text{M}^+ - \text{CONaphCl}$), 189 ($\text{M}^+ - \text{PhCONaphCl}$), 161 ($\text{M}^+ - \text{COPhCONaphCl}$).

POLYMER SYNTHESIS

Polymerizations were typically carried out in dry, 50 mL three-neck round bottom flasks equipped with stirring, a Dean Stark trap fitted with a condensor, and a Nitrogen purge inlet according to the following methods A-F:

Method A (a typical procedure): The 3-neck round bottom flask was charged with 1,4bis-(4'-fluoro-1'-naphthoyl) benzene (1.27 g; 3.00 mmol), BPA (684 mg; 3.00 mmol), K_2CO_3 (829 mg; 6.00 mmol) chlorobenzene (10 mL), and $TMSO_2$ (6 mL-9 mL, 35% - 20% w/v). With stirring, the system temperature was raised to 210 °C and maintained for 3-6 h. Any water formed in the reaction was removed with the chlorobenzene at 100-140 °C. As the reaction mixture was becoming more viscous, the growing molecular weight was monitored by GPC. At the point at which the molecular weight began to decrease, the reaction was stopped. The polymer was quantitatively poured into stirring methanol (200 mL) containing 2-3 drops of conc. HCl. The resulting stringy polymer was redissolved in chloroform, filtered through a thin pad of celite, and reverse precipitated for the removal of any low molecular weight fractions; yielding yellow, fibrous polymer.

Method B (a typical procedure): The 3-neck round bottom flask was charged with 1,4-bis(4'-fluoro-1'-naphthoyl) benzene (1.27 g, 3.00 mmol), DP (559 mg, 3.00 mmol), K_2CO_3 (829 mg, 6.00 mmol), chlorobenzene (10 mL), and N-methyl-caprolactam (6 mL - 9 mL, 30%-20% w/v). With stirring, the temperature was raised to 240 °C and maintained for 3-5 h. Any water formed in the reaction was removed with chlorobenzene at 100-140 °C. As the reaction mixture was becoming more viscous, the growing molecular weight was monitored by GPC. At the point at which the molecular weight decreased, the reaction was stopped. The polymer was quantitatively poured into stirring methanol (200 mL) containig 2-3 drops of conc. HCl. The powdery polymer was

filtered, followed by a 1 h reflux in fresh water, methanol, and chloroform respectively. The product was dried in a vacuum oven at 100 °C for 12 h.

Method C (a typical procedure): The 3-neck round bottom flask was charged with 1,4bis-(4'-fluoro-1'-naphthoyl) benzene (1.27 g, 3.00 mmol), HQ (330 mg, 3.00 mmol), K_2CO_3 (289 mg, 6.00 mmol), chlorobenzene (10 mL), and diphenylsulfone (7.82 g, 20% w/v). With stirring, the reaction temperature was raised to 300 °C and maintained for 2-3 h. Any water formed in the reaction was removed with chlorobenzene at 100-140 °C. The polymer was not soluble in chloroform so GPC monitoring of the reaction was not possible. When the viscosity of the polymer (apparently) decreased, The reaction mixture was poured into stirring methanol (200 mL) containing 2-3 drops of conc. HCl. The spaghetti-like material was crushed up and relaxed for 1 h in acetone and chloroform respectively. The polymer was filtered and dried in a vacuum oven at 100 °C for 12 h.

Method D (a typical procedure): The 3-neck round bottom flask was charged with 1,4bis(4'-fluoro-1'-naphthoyl) benzene (1.27 g, 3.00 mmol), HQ (330 mg, 3.00 mmol), K_2CO_3 (829 mg, 6.00 mmol), toluene (15 mL), and NMP (8 mL, 20% w/v). With stirring, the reaction temperature was raised to 140 °C and maintained for 1 h until all the water formed during the reaction was removed with the toluene. The temperature was then raised to 200 °C (as the reaction showed some solubility problems at 180 °C) and maintained for 3 h. Monitoring of the molecular weight by GPC was not possible as the oligomers were not soluble in chloroform. The polymer was refluxed in methanol and chloroform and were dried in a vacuum at 100 °C for 12 h.

Method E (a typical procedure): The 3-neck round bottom flask was charged with 4-chloro-1-(4'-fluoro-1'-naphthoyl) naphthalene (1.00 g, 3.00 mmol), HQ (330 mg, 3.00 mmol), K_2CO_3 (829 mg, 6.00 mmol), toluene (30 mL), and $TMSO_2$ (4.8 mL, 28% w/v). With stirring, the reaction temperature was raised to 140-150 °C and held for 1 h. During this time, any water formed in the reaction was removed with toluene and fresh deoxygenated toluene was introduced to the system. The temperature was then raised to

180 °C and maintained for 2 h. As the reaction mixture became more viscous, the growing molecular weight was monitored by GPC until there was a drop; at which time, the reaction was stopped. The polymer was poured into stirring methanol (200 mL) containing 2-3 drops conc. HCl. The spaghetti-like polymer was redissolved in chloroform, filtered through a thin pad of celite, and then reverse precipitated yielding yellow fibrous polymer.

Method F (a typical procedure): The 3-neck round bottom flask was charged with 1,4-bis(4'-fluoro-1'-naphthoyl) benzene (845 mg; 2.00 mmol), 1,4-bis(4'-chloro-1'-naphthoyl) benzene (908 mg, 2.00 mmol), BPA (913 mg; 4.00 mmol), K₂CO₃ (719 mg; 5.21 mmol) chlorobenzene (15 mL), and TMSO₂ (7.5 mL-13.5 mL, 35% - 20% w/v). With stirring, the system temperature was raised to 210 °C and maintained for 3-6 h. Any water formed in the reaction was removed with the chlorobenzene at 100-140 °C. As the reaction mixture was becoming more viscous, the growing molecular weight was monitored by GPC. At the point at which the molecular weight began to decrease, the reaction was stopped and quantitatively poured into stirring methanol containing 2-3 drops of conc. HCl. The precipitate was redissolved in CHCl₃, filtered through a pad of celite, and reverse precipitated yielding yellow powdery polymer.

PURIFICATION OF POLYMERS BY REVERSE PRECIPITATION

The polymer (1.0 g) was dissolved in chloroform (40 mL) with stirring. To the chloroform solution, methanol was added dropwise through a dropping funnel to the point at which the polymer had precipitated out as a gummy residue. The addition was then stopped and the polymer redissolved in a minimal amount of chloroform and precipitated into methanol. If the chloroform solution was too concentrated, the precipitate took the form of a ball and the mother solution was diluted appropriately. If the solution was too dilute, the precipitate was powdery and the mother solution

concentrated. If the solution was of the correct concentration, a fibrous polymer resulted which was filtered and dried in a vacuum oven at 80 °C for several hours.

Polymer Data - Monoketone

III-2a: IR (film, cm^{-1}) 1648.7 (C=O), 1238.0 (C-O-C), ^1H NMR (400 MHz) 8.60 (d, 1H, $J_{\text{H-H}} = 8.2$ Hz), 8.38 (d, 1H, $J_{\text{H-H}} = 8.1$ Hz), 7.55 (m, 2H), 7.45 (d, 1H, $J_{\text{H-H}} = 8.1$ Hz), 7.21 (d, 1H, $J_{\text{H-H}} = 8.6$ Hz), 6.98 (d, 1H, $J_{\text{H-H}} = 8.6$ Hz), 6.65 (d, 1H, $J_{\text{H-H}} = 8.0$ Hz), 1.65 (s, 6H), ^{13}C NMR (100 MHz) 198.05, 157.29, 153.83, 146.73, 133.05, 131.74, 131.71, 128.53, 128.32, 126.41, 126.05, 122.31, 119.60, 109.02, 42.32, 30.96.

III-2b: IR (film, cm^{-1}) 1654.1 (C=O), 1239.3 (C-O-C), 1175.7 (C-F), ^1H NMR (400 MHz) 8.65 (d, 1H, $J_{\text{H-H}} = 8.2$ Hz), 8.35 (d, 1H, $J_{\text{H-H}} = 7.8$ Hz), 7.63 (m, 3H), 7.43 (d, 1H, $J_{\text{H-H}} = 8.4$ Hz), 7.11 (d, 1H, $J_{\text{H-H}} = 8.9$ Hz), 6.86 (d, 1H, $J_{\text{H-H}} = 8.0$ Hz), ^{13}C NMR (100 MHz) 197.93, 157.19, 155.89, 133.15, 132.84, 132.01, 128.78, 126.83, 126.19, 125.59, 122.25, 118.84, 110.98.

III-2c: IR (film, cm^{-1}) 1654.2 (C=O), 1239.9 (C-O-C), ^1H NMR (400 MHz, CHCl_3) 8.61 (d, 1H, $J_{\text{H-H}} = 8.4$ Hz), 8.37 (d, 1H, $J_{\text{H-H}} = 8.0$ Hz), 7.74 (d, 1H, $J_{\text{H-H}} = 7.4$ Hz), 7.56 (m, 2H), 7.42 (d, 1H, $J_{\text{H-H}} = 6.9$ Hz), 7.39 (d, 1H, $J_{\text{H-H}} = 7.5$ Hz), 7.34 (t, 1H, $J_{\text{H-H}} = 7.4$ Hz), 7.25 (t, 1H, $J_{\text{H-H}} = 7.6$ Hz), 7.22 (d, 1H, $J_{\text{H-H}} = 8.7$ Hz), 6.95 (d, 1H, $J_{\text{H-H}} = 8.6$ Hz), 6.65 (d, 1H, $J_{\text{H-H}} = 8.0$ Hz), ^{13}C NMR (100 MHz) 197.96, 156.92, 154.94, 150.98, 141.87, 140.01, 133.04, 131.92, 131.61, 129.69, 128.54, 127.85, 127.71, 127.50, 126.47, 126.06, 126.00, 122.26, 120.33, 119.65, 109.44, 64.49.

Polymer data - Diketone

III-1a: IR (film, cm^{-1}) 1654.4 (C=O), 1239.1 (C-O-C), ^1H NMR (400 MHz) 8.41 (m, 2H), 7.86 (s, 2H), 7.56 (m, 2H), 7.50 (d, 1H, $J_{\text{H-H}} = 8.0$ Hz), 7.28 (d, 1H, $J_{\text{H-H}} = 8.6$ Hz), 7.05 (d, 1H, $J_{\text{H-H}} = 8.5$ Hz), 6.76 (d, 1H, $J_{\text{H-H}} = 8.0$ Hz), ^{13}C NMR (100 MHz) 196.43, 157.51, 153.81, 149.91, 142.27, 132.91, 130.97, 130.15, 129.43, 128.56, 127.88, 126.58, 126.51, 125.81, 122.43, 119.73, 108.80, 42.43, 31.03.

III-1b: IR (film, cm^{-1}) 1657.8 (C=O), 1243.8 (C-O-C), ^1H NMR (400 MHz) 8.35 (d, d, 2H, $J_{\text{H-H}} = 8.0$ Hz, $^4J_{\text{H-H}} = 1.6$ Hz), 7.90 (s, 2H), 7.58 (m, 3H), 7.44 (d, 1H, $J_{\text{H-H}} = 8.4$ Hz), 7.12 (d, 1H, $J_{\text{H-H}} = 9.2$ Hz), 6.93 (d, 1H, $J_{\text{H-H}} = 8.0$ Hz), ^{13}C NMR (100 MHz) 196.35, 157.18, 155.86, 142.10, 132.95, 132.08, 130.83, 130.27, 130.16, 128.86, 128.68, 126.95, 126.87, 125.92, 125.61, 122.76, 122.32, 118.87, 110.88.

III-1e: IR (film, cm^{-1}) 1654.5 (C=O), 1238.2 (C-O-C), ^1H NMR (400 MHz, CDCl_3) 8.35 (d, 2H, $J_{\text{H-H}} = 8.1$ Hz), 7.82 (s, 2H), 7.74 (d, 1H, $J_{\text{H-H}} = 7.6$ Hz), 7.55 (m, 2H), 7.44 (d, 1H, $J_{\text{H-H}} = 8.1$ Hz), 7.41 (d, 1H, $J_{\text{H-H}} = 7.5$ Hz), 7.35 (t, 1H, $J_{\text{H-H}} = 7.4$ Hz), 7.25 (m, 2H), 6.98 (d, 1H, $J_{\text{H-H}} = 8.8$ Hz), 6.73 (d, 1H, $J_{\text{H-H}} = 8.0$ Hz), ^{13}C NMR (100 MHz) 196.38, 157.11, 154.87, 150.99, 142.20, 142.04, 140.07, 132.87, 130.80, 130.04, 129.78, 129.36, 128.56, 127.91, 127.79, 126.62, 126.53, 126.05, 125.79, 122.37, 120.40, 119.78, 109.19.

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