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

by

ANNE LE GUEN, B.Sc.

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

The Department of Chemistry

Carleton University

Ottawa, Ontario, Canada

August, 1994

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

submitted by

ANNE LE GUEN, B.Sc.

in partial fulfilment of the requirements
for the degree of Master of Science

Prof. Z. Y. Wang, Thesis Supervisor

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

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August, 1994

ABSTRACT

In the course of studying correlations between structure-properties of polymers, high molecular weight, amorphous, soluble poly(arylene ether ketone)s were synthesized from 1,8-bis(4-fluorobenzoyl)naphthalene and a variety of aromatic bisphenols. The polymers were characterized by gel permeation chromatography and by ^1H and ^{13}C NMR. Glass transition temperatures, measured by differential scanning calorimetry, ranged from 214 to 274 $^{\circ}\text{C}$. The 5 % weight loss of these polymers by thermogravimetry occurred all above 476 $^{\circ}\text{C}$ in nitrogen and 478 $^{\circ}\text{C}$ in air.

Transformation of the poly(arylene ether ketone)s synthesized to the acenaphthylene-based polyethers was also attempted and gave unexpected results. The deoxy-olefination, run at either low or high concentration with the Lawesson's reagent, resulted in the formation of the cross-linked or non-cross-linked polymers, respectively. Sulfur was proved to be present in the cyclized polymers, but the polymer structures could not be detailed.

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SYMBOLS AND ABBREVIATIONS

BPA	Bisphenol A or 4,4'-Isopropylidenediphenol
COSY	Correlated spectroscopy
DMAc	N,N-dimethylacetamide
DMSO	Dimethyl sulfoxide
DSC	Differential scanning calorimetry
E'	Young's modulus
GPC	Gel permeation chromatography
HETCOR	Heteronuclear shift correlation
IR	Infrared
J	Coupling constant (Hz)
MS	Mass spectrometry
M _n	Number-average molecular weight
M _w	Weight-average molecular weight
n	Number of 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
TCE	1,1,2,2-Tetrachloroethane
T _d	Decomposition temperature
T _g	Glass transition temperature
TG	Thermogravimetry
THF	Tetrahydrofuran
TLC	Thin layer chromatography
T _m	Melting temperature
TMA	Thermomechanical analysis
TMSO ₂	Tetramethylene sulfone
UV	Ultraviolet
δ	Chemical shift (ppm)
η _{inh}	Inherent viscosity

CHAPTER I. Introduction

The terms heat-resistant and thermally-stable, used synonymously with high-temperature polymers, refer to a high-performance polymer which maintains useful properties for a stated period of time at elevated temperatures. High-performance polymers are best presented by their properties. They have high thermal stability (e.g., continuous use temperatures above 150 °C over 50,000 hours), excellent mechanical strength per unit weight, chemical resistance at elevated temperatures, and good electrical properties (e.g., as insulators). The quest for high-temperature organic polymers began in the late fifties primarily to meet the demands of the aerospace and electronics industries. Currently, high-temperature polymers are used or considered for use in functional and structural applications in the aerospace, automotive, and electronics industries.

The prerequisite for a high-performance polymer usually include (a) high melting and softening points for highly crystalline polymers or amorphous and semicrystalline polymers, (b) a low weight loss at elevated temperatures as determined by thermogravimetry, (c) chemical inertness especially to oxygen, moisture, acids and bases, and (d) specific properties such as high tensile modulus and low dielectric constants in the desired temperature range.¹

Both chemical and physical factors determine the heat resistance of polymers. The strength of the primary bonds in the polymer is the single most important determinant for the heat resistance.² This is especially critical with respect to the bonds in the polymer backbone. Breakage of those bonds results in deterioration of mechanical strength due to the drop in molecular weight. Thus the characteristic structures of thermally stable polymers usually include aromatic, heteroaromatic, and fused rings as a major portion of the polymer composition. Commercial poly(p-phenylene) is one example. It has a high T_m of 530 °C and is stable up to 660 °C without any weight loss.

¹ S. R. Sandler and W. Karo, *Polymer Syntheses*, 1992, 2nd Ed, Vol I, 254.

² G. Odian, *Principles of polymerization*, 1991, 3rd Ed, 150.

Figure I.1. Poly(p-phenylene)

However, because of its high melting and high crystallinity, it is also impossible to be melt or solution processed. It is only marketed as a laminating resin by Monsanto. The inherent intractability and insolubility of these polymers severely restrict processing and consequently limit the commercial significance of these high-temperature polymers. Therefore, inclusion of other functionalities such as ether, sulfone, imide or amide, in the polymer chains has been studied in order to improve solubility and processability of those heat-resistant polymers.

I.1. Poly(arylene ether ketone)s

One class of high-performance polymers that has received considerable attention is the poly(arylene ether)s. These thermoplastic polymers offer an attractive combination of chemical, physical and mechanical properties. Since early research in the late fifties, several poly(arylene ether)s such as Udel (polysulfone), PEEK [poly(ether ether ketone)] and Victrex PES (polyethersulfone) have become commercially available (Figure I.2). These high-performance engineering thermoplastics are used in a variety of applications such as adhesives, coatings, composite matrices, moldings, toughening agents and ultrafiltration membranes.³

³ P. M. Hergenrother, *Polymer Journal*, 1987, 19 (1), 73.

Figure I.2. Udel, PEEK and PES Polymers.

Among those polymers, poly(arylene ether ketone)s are a desirable class of polymers, due to their extremely high thermal stability, good solvent resistance, and excellent mechanical strength. They comprise the class of polymers in which arylene groups are linked by ether and carbonyl groups. One of well-recognized poly(arylene ether ketone) is called PEEK (Figure I.2) which has been described as a tough, crystalline thermoplastic. It also shows good chemical resistance and good dielectric properties, even at high temperatures, as well as almost no flammability and among the lowest levels of smoke and gas emission during combustion.⁴ This polymer was first produced by Imperial Chemical Industries PLC in the late seventies and was commercialized in 1981 under the trade name Victrex. PEEK is used over a wide range of applications in electrical, electronics, aerospace, automotive, and oil industries.⁵

Poly(arylene ether ketone)s are usually crystalline and are therefore resistant to attack by solvent. The only room-temperature solvent known for PEEK is concentrated sulfuric acid. However, while the crystallinity gives poly(arylene ether ketone)s a unique set of properties among all engineering thermoplastics, the low solubility coupled with high

⁴ M. S. Reisch, *Chemical and Engineering News*, 1989, Sept. 4, 21.

⁵ H. F. Mark, N. M. Bikales, C. G. Overberger and G. Menges, *Encyclopedia of Polymer Science and Engineering*, 1985, 2nd Ed, 12, 313.

melting points generally above 300 °C hampers their synthesis. The nucleophilic displacement and the Friedel-Craft reactions leading to crystalline poly(arylene ether ketone)s, as reported in the late sixties, were run at very high temperatures (>300 °C) or in strongly acidic media in which the carbonyl groups are protonated, allowing the growing polymer to remain in solution.⁶ In contrast, an amorphous nature of poly(arylene ether ketone)s allows the polymerization run under milder conditions. Crystallinity is usually expected when the polymer backbone is built up with *para*-disubstituted benzene rings. Relatively small changes in the structure, such as substitution of methylene for carbonyl⁷ or *ortho* and *meta* linkages in the chain,⁸ can prevent crystallization. Thus, it is possible to predict to a certain extent whether the polymer formed will be crystalline or amorphous in order to ease the synthesis.

I.2. Synthetic Routes to Poly(arylene ether ketone)s

There are mainly two synthetic routes to the construction of poly(arylene ether ketone)s. One involves the nucleophilic displacement reaction using a bisphenol and an activated dihaloarene as a pair of monomers. The polymer is constructed via the formation of the ether bond. The electrophilic substitution is another polymer forming reaction. A diacid or its chloride and an electron-rich arene as monomers are condensed to produce a polymer through the formation of a keto function.

I.2.1. Nucleophilic Displacement Polycondensation

For the past 25 years, the nucleophilic displacement reaction has been used to synthesize high molecular weight poly(arylene ether ketone)s. In a nucleophilic aromatic displacement polymerization, a bisphenol is converted to a reactive bisphenoxide upon

⁶ R. N. Johnson, A. G. Farnham, R. A. Clendinning, W. F. Hale and C. N. Merriam, *J. Polym. Sci. Part A-1*, 1967, 5, 2375

⁷ H. R. Kircheldorf, *Handbook of Polymer Synthesis Part A*, 1992, 574.

⁸ G. Allen and J. C. Bevington, *Comprehensive Polymer Science*, 1989, 5, 483.

reaction with a base. It then reacts with an aromatic dihalide to yield a linear polymer via the formation of aryl ether linkages. In general, dipolar aprotic solvents such as dimethylsulfoxide (DMSO), N-methylpyrrolidinone (NMP), N,N-dimethylacetamide (DMAc) or tetramethylenesulfone (TMSO₂) enhance the reaction rate by solvating the ions, increasing the nucleophilicity of the bisphenoxide, and solubilizing any intermediates formed.

The first synthesis of poly(arylene ether ketone)s by nucleophilic displacement was carried out with 50% aqueous sodium hydroxide as a base and chlorobenzene as an azeotroping agent in DMSO.⁶ But side reactions between DMSO and the hydroxide anion led to the use of different solvents such as NMP, DMAc, or TMSO₂ and weaker bases such as anhydrous potassium carbonate.⁹ An advantage to using potassium carbonate is that the stoichiometry needs not to be carefully controlled, an excess of base can be used without any hydrolytic side reactions. Also, all reagents can then be added together and the polymerization can be run with simultaneous dehydration.

An exact stoichiometric balance and the high purity of two monomers are necessary to achieve high molecular weights. If some monofunctional impure or excess of one monomer is present, the molecular weight will be limited due to rendering the chain end inactive.

The formation of the ether linkage occurs by a two-step S_NAr mechanism (Scheme I.1).¹⁰ The first step involves the reaction of a phenoxide anion with an activated halide to form the Meisenheimer complex. In a second step, the halide anion (X⁻) is eliminated to form the product or the phenoxide ion dissociates to regenerate the starting material. The reactivity of the dihalide depends not only on the electron-withdrawing ability of the activating group, but also on the halide itself. The order of reactivity for the halides is

⁹ R. Viswanathan, B. C. Johnson and J. E. Mc Grath, *Polymer*, 1984, 25, 1827.

¹⁰ V. Percec, R. S. Clough, J. Fanjul and M. Grigoros, *Polym. Preprints*, 1993, 34 (1), 162.

found as $F \gg Cl > Br \sim I$. The difference in reactivity between the fluoride and other halides can be accounted for the greater electronegativity of fluorine atom which makes its adjacent carbon relatively more positive charged or more reactive towards a nucleophile.¹¹ Furthermore, the Meisenheimer complex is more stabilized because the fluorine attracts more negative charge generated than other halides. Finally, since the fluorine has the smallest atomic radius, it provides the least steric hindrance to the phenoxide during nucleophilic displacement. Therefore, the Meisenheimer complex is easily formed and the rate determining step is then the expulsion of the fluoride anion.

Scheme I.1. Mechanism of nucleophilic substitution.

I.2.2. Electrophilic Substitution Polycondensation

The oldest synthesis of poly(arylene ether ketone)s involved a Friedel-Crafts polyacylation, using diphenyl ether and isophthalic acid dichloride in nitrobenzene with aluminum chloride as a catalyst, which gave only a low molecular weight material. Since then, different solvent-catalyst systems have been investigated in order to obtain linear high molecular weight poly(arylene ether ketone)s.

The mechanism is assumed to proceed conventionally by attack of aryl acylium ions on reactive phenyl groups (Scheme I.2). The substrates containing electron-

¹¹ V. Percec, R. S. Clough, P. L. Rinaldi and V. E. Litman, *Macromolecules*, 1991, 24, 21.

withdrawing groups like benzophenone and 1,4-dibenzoylbenzene or benzene itself prevent the double acylation reaction at both ends and therefore are not suitable co-monomers.

Scheme I.2. Mechanism of electrophilic substitution.

AB-type monomers containing both acyl chloride and phenoxy group can be condensed in the presence of Lewis acids such as $AlCl_3$ or BF_3 . But, in normal Friedel-Crafts solvents such as carbon disulfide, dichloromethane or nitrobenzene, crystallization and precipitation of oligomers likely occur, which prevents the formation of high molecular weight polymers. Thus, the use of liquid HF , which is a good solvent for poly(ether ketone)s, with BF_3 as a catalyst allowed the synthesis of high molecular weight polymers. Nevertheless, this approach also has limitations such as the formation of cross-linking within the polymer and the use of relatively expensive, aggressive and poisonous reaction medium.⁷ The use of excess of $AlCl_3$ as a catalyst plus a Lewis base to moderate the activity of the catalyst and a conventional solvent such as 1,2-dichloroethane also gave good results. The Lewis base appears to form a complex with $AlCl_3$ which acts as a solvent for the polymer- $AlCl_3$ complex during the polymerization thereby maintaining the

polymer in solution.¹² Thus this method appears commercially viable although requiring the use and disposal of large amounts of aluminum chloride.

Another approach utilizes the solvating power and catalytic activity of trifluoromethanesulfonic acid (triflic acid).¹³ This superacid prompts the acylation reaction with acids or acid chlorides at room temperature and also allows the preparation of poly(ether ketone)s at moderate temperatures. The formation of poly(ether ketone)s takes place even when free acids instead of acid chlorides are used.

Aromatic poly(ether ketone)s of high molecular weight can also be prepared readily by direct polycondensation of dicarboxylic acids containing phenylether structures with diphenoxybenzene¹⁴ or by self-polycondensation of various AB monomers containing benzoic acid and phenylether structures in phosphorus pentoxide-methane sulfonic acid¹⁵ as condensing agent and solvent.

Thus, the development of efficient and mild methods for the synthesis of poly(arylene ether ketone)s by electrophilic condensation still is a significant aspect of synthetic polymer chemistry.

I.3. Glass Transition Temperature

Polymeric materials are characterized by two major types of transition temperature, the crystalline melting temperature (T_m) and the glass transition temperature (T_g). The T_m is the melting temperature of crystalline domains of a polymer sample. Whereas the T_g is the temperature at which the amorphous domains of a polymer take on characteristic properties of the glassy state, e.g. brittleness, stiffness and rigidity.

¹² J. B. Rose, *Recent Advances in Mechanistic and Synthetic Aspects of Polymerization*, 1987, 207.

¹³ H. M. Colquhoun and D. F. Lewis, *Polymer*, 1988, 29, 1902.

¹⁴ M. Ueda and M. Sato, *Macromolecules*, 1987, 20, 2675.

¹⁵ M. Ueda and M. Oda, *Polymer Journal*, 1989, 21(9), 673.

When cooling a polymeric material from the liquid or rubbery state, if certain symmetry requirements are met, the macromolecules are able to pack into an ordered, lattice arrangement and crystallization occurs. However, not all polymers are sufficiently regular along their length to allow the formation of crystalline lattices. Thus, when the polymer fails to crystallize, the amorphous, liquid-like structure of the polymer is retained. As the temperature is lowered, the movement becomes progressively slower until eventually the available thermal energy is insufficient to overcome the rotational energy barriers in the chain.¹⁶ At this temperature, which is known as the T_g , the chains become locked in the conformation they possessed when the T_g was reached. Below the T_g , the polymer is in the glassy state and is, in effect, a frozen liquid with a completely random structure. The T_g can be easily measured from the change in many properties of the material such as specific volume, heat capacity and modulus. Whether a polymer sample exhibits both thermal transitions, like semi-crystalline polymers, or only one, for crystalline polymers (T_m) and amorphous polymers (T_g), depends on its morphology. But the opportunities for any irregularity along the chain are numerous and the crystallization rate is inherently slow, the formation of glassy state is common in polymers.

Many factors can affect the glass transition temperature. For high molecular weight polymers, the T_g is essentially independent of molecular weight, but as the polymer chain length becomes shorter, the T_g is likely to decrease appreciably. This lowering of the T_g is essentially an end-group effect, the two ends of the polymer chain being able to move about more freely than a segment in the chain interior.¹⁷ Thus, the high molecular weight is a prerequisite for obtaining the reproducible T_g of polymer.

The polymer structure also greatly affects the T_g . The chain mobility of the polymer backbone is undoubtedly the most important factor influencing the T_g . A flexible chain will

¹⁶ J. M. Cowie, *Polymers: Chemistry and physics of modern materials*, 1991, 2nd Ed, 256.

¹⁷ R. J. Roe, *Encyclopedia of Polymer Science and Engineering*, 1985, 2nd Ed, 7, 531.

have a low T_g whereas a rigid chain will result in a high T_g . Also, the bulkier the substituent on the polymer backbone, the less will be the rotational freedom and the higher the T_g .¹⁸ Superimposed on this group size factor are the effects of polarity and flexibility of the pendant group itself. Polar groups, for example, tend to encourage a higher T_g than non-polar groups of similar size due to an increase in dipole-dipole interaction.

Therefore, the glass transition temperature range of polymers can to a certain extent be predicted. By varying the structure of a polymer, one can obtain the desired thermal properties.

I.4. Design of Monomers and Polymers

Even though the correlations between structure-properties are not fully understood, some general guiding principles linking the properties to the molecular structure have been well developed as useful tools in synthesizing polymeric materials with the designed properties. Therefore, with understanding of the correlation between the structure and the glass transition temperature of known poly(arylene ether ketone)s, it is possible to design new polymers with improved thermal properties.

Structurally related poly(arylene ether ketone)s such as those containing groups A^{19,20} and B^{21,22,23,24} (Figure I.3) have been synthesized by several groups, which allow systematical studies and comparisons of their glass transition temperatures (T_g s), thermal stabilities and mechanical properties. Depending on the substitution patterns of A

¹⁸ M. P. Stevens, *Polymer Chemistry; an Introduction*, 1990, 2nd Ed, 80.

¹⁹ P. M. Hergenrother, B. J. Jensen and S. Havens, *Polymer*, 1988, 29, 358.

²⁰ R. Singh and A. S. Hay, *Macromolecules*, 1992, 25, 1017.

²¹ Z. Y. Wang and C. Zhang, *Macromolecules*, 1993, 26, 3324.

²² A. Bhatnagar, R. S. Mani, R. S. Weeks and D. K. Mohanty, *J. Mater. Chem.*, 1991, 1(6), 977.

²³ A. Bhatnagar, R. S. Mani, R. S. Weeks and D. K. Mohanty, *Makromol. Chem.*, 1993, 144, 1935.

²⁴ A. Bhatnagar, R. S. Mani, R. S. Weeks and D. K. Mohanty, *Polymer Journal*, 1994, 26 (4), 403.

and B, the Tgs of isomeric polymers vary. For example, three isomeric poly(arylene ether ketone)s containing the phenylenedicarboxyl units (A) have Tgs varying in the order as 1,2- > 1,4- > 1,3-substitutions. Similar effect is also seen in the series of poly(arylene ether ketone)s having isomeric biphenylenedicarboxyl groups B, for Tgs varying in the order as 4,4'- > 2,2'- > 3,3'-substitutions. The relatively high Tgs for the less linear polymers with *ortho*-substituted aryls can be attributed to enhanced chain stiffness caused by the restricted rotation of the adjacent benzoyl groups.

Figure I.3. Isomeric poly(arylene ether ketone)s.

As part of ongoing systematical studies of the effects of structural symmetry or substitution pattern of the arylene core in poly(arylene ether ketone)s on the polymer properties, isomeric naphthalene-based poly(arylene ether ketone)s (C, Figure I.3) are the subject of preparation and evaluation. In spite of much work on the synthesis of new poly(ether ketone)s, only those containing 2,6-naphthylenedicarboxylic units are known.¹⁹ Introduction of the naphthylene moiety in the polymer showed an increase in the Tg as compared to analogous phenylene-containing poly(ether ketone)s. Substitution with methyl groups at 1,5-positions of the 2,6-naphthylenedicarboxylic unit improved the solubility, increased the Tg, but decreased thermooxidative stability.²⁵ Among a dozen of possible isomeric naphthylenedicarboxyls, the 1,8-isomer is quite unique. Two benzoyl groups at the *peri* positions of naphthalene are almost as crowded as those in other *ortho*-

²⁵ M. Ohno, T. Takata, T. Endo, *Macromolecules*, 1994, 27, 3447.

the *peri* positions of naphthalene are almost as crowded as those in other *ortho*-isomers (e.g., 1,2- and 2,3-isomers), which is expected to increase the Tgs of poly(arylene ether ketone)s in the same way as 1,2-phenylene- and 2,2'-biphenylenedicarboxyl groups do. In addition, the 1,8-naphthylenedicarboxyl unit should be able to undergo an intramolecular deoxy-olefination reaction to yield acenaphthylene unit. Such polymer transformation would allow the easy preparation of a series of novel acenaphthylene-based polyethers from readily available naphthalene-based poly(ether ketone)s.

CHAPTER II. Synthesis of Monomer: 1,8-Bis(4-fluorobenzoyl)naphthalene

Three different pathways were studied for the synthesis of the target monomer, 1,8-bis(4-fluorobenzoyl)naphthalene (Scheme II.1):

- Friedel-Crafts acylation of 1,8-naphthalic anhydride,
- Grignard reaction with 1,8-naphthalic anhydride,
- Grignard reaction with acenaphthenequinone.

The first two routes involved an electrophilic and nucleophilic reaction with 1,8-naphthalic anhydride, a cheap and readily available material, to yield a monosubstituted carboxylic acid. A transformation of the acid to the acyl chloride would then enable a second electrophilic substitution to yield the desired monomer. The use of acenaphthenequinone in the third pathway allowed the double addition of the Grignard reagent in one step. The resulting diol would then be easily oxidized to yield the expected diketo monomer. The last approach was found to be the most effective one leading to the monomer in high yield.

Scheme II.1. Possible routes to the monomer.

II.1. Friedel-Crafts Acylation

Acid anhydrides are known to react with aromatic compounds in the presence of anhydrous aluminum chloride via the Friedel-Crafts reaction.²⁶ The use of acid anhydrides in place of the corresponding acid chlorides offers certain advantages including the greater ease of obtaining pure anhydrides, their availability as commercial products and a smooth reaction in good yields.²⁷ The reaction of phthalic anhydride with fluorobenzene was reported to yield 4-(4-fluorobenzoyl)benzoic acid.²⁸ Also, the reaction of 1,2-naphthalic anhydride with fluorobenzene yielded a mixture of 2-(4-fluorobenzoyl)-1-naphthoic acid and 1-(4-fluorobenzoyl)-2-naphthoic acid.²⁹ Therefore, the same success was expected from the reaction with 1,8-naphthalic anhydride.

The reaction was attempted using a 2.5:1 molar ratio of aluminum chloride to 1,8-naphthalic anhydride. Fluorobenzene in excess was used as a reagent and a solvent but did not dissolve 1,8-naphthalic anhydride. 1,1,2,2-Tetrachloroethane and nitromethane also failed to dissolve 1,8-naphthalic anhydride, while hot nitrobenzene was found to be a good solvent. Thus nitrobenzene was added to the hot mixture until complete dissolution of the reagents. In spite of that, after one day of reaction, TLC showed no consumption of the starting material. Mason³⁰ already attempted the condensation between 1,8-naphthalic anhydride and benzene using varying reaction conditions. Even though the reaction mixture turned dark upon action of aluminum chloride with the anhydride in nitrobenzene, the anhydride was recovered almost quantitatively. Thus the acylium ion formed from 1,8-naphthalic anhydride seems not reactive enough as an electrophile. This reaction pathway was not studied any further.

²⁶ E. Berliner, *Organic Reactions*, 1962, V, 229.

²⁷ B. S. Furniss, A. J. Hannaford, P. W. Smith and A. R. Tatchell, *Vogel's textbook of practical organic chemistry*, 1989, 5th Ed., 1006.

²⁸ F. C. Hahn and E. E. Reid, *J. Am. Chem. Soc.*, 1924, 46, 1645.

²⁹ M. S. Newman, S. Swaminathan and R. Chatterji, *J. Am. Chem. Soc.*, 1959, 24, 1961.

³⁰ F. A. Mason, *J. Am. Chem. Soc.*, 1924, 125, 2119.

II.2. Grignard Reaction with 1,8-Naphthalic anhydride

The mixture of 1-(4-fluorobenzoyl)-2-naphthoic acid and 2-(4-fluorobenzoyl)-1-naphthoic acid was obtained from the Grignard reaction of 4-fluorophenylmagnesium bromide with 1,2-naphthalic anhydride.²⁹ The reaction of 1,8-naphthalic anhydride with phenyl or tolylmagnesium bromide was reported to yield the expected 8-benzoyl-1-naphthoic acid and 8-(4-methylbenzoyl)-1-naphthoic acid respectively.³¹ Also 8-(4-bromobenzoyl)-1-naphthoic acid was obtained by the same method.³² Therefore the Grignard reaction of 1,8-naphthalic anhydride and 4-fluorophenylmagnesium bromide was attempted in a 1:1.1 molar ratio under similar reaction conditions (route b, Scheme II.1). The Grignard reagent in THF was added dropwise to a solution of 1,8-naphthalic anhydride in THF over two hours. TLC (chloroform as an eluent) showed the immediate consumption of the starting material. After hydrolysis of the mixture and usual acid-base washings, recrystallization twice from toluene gave 8-(4-fluorobenzoyl)-1-naphthoic acid as white crystals in good yield. The purity of the product was confirmed by TLC analysis and a constant melting point.

Deuterated acetone, DMSO, and methanol were used as solvents for measuring the ^1H and ^{13}C NMR spectra. Unfortunately, the spectra showed broad peaks which made the analysis quite difficult. In addition, no carbonyl peak was seen in the ^{13}C NMR spectrum. This acid was actually reported to exist in solution as a mixture of tautomers (Scheme II.2)^{32,33,34,35} which would account for the poor resolution and the absence of carbonyl

³¹ D. V. Nightingale, W. S. Wagner and R. H. Wise, *J. Am. Chem. Soc.*, **1953**, *75*, 4701.

³² D. P. Weeks and G. W. Zuorick, *J. Am. Chem. Soc.*, **1969**, *91*, 477.

³³ H. E. French and J. E. Kircher, *J. Am. Chem. Soc.*, **1944**, *66*, 298.

³⁴ P. R. Jones and A. A. Lavigne, *J. Org. Chem.*, **1960**, *25*, 2020.

³⁵ K. Bowden and A. M. Last, *J. Chem. Soc. Perkin II*, **1973**, *8*, 1144.

peak in the ^{13}C NMR spectrum.³⁶ The cyclic form is supposed to be predominant in non polar solvents^{32,33} but 8-(4-fluorobenzoyl)-1-naphthoic acid was only slightly soluble in chloroform and dichloromethane. Thus IR and MS were used to confirm the structure of the acid. The IR spectrum showed only one absorption in the carbonyl region (1682 cm^{-1}) and an hydroxy peak at 3301 cm^{-1} (Figure II.1). This might be accounted for the fact that in the solid state, 8-(4-fluorobenzoyl)-1-naphthoic acid exists in the cyclic form essentially.³² Thus, the absorption at 1686 cm^{-1} would result from the lactone carbonyl of the ring tautomer. The parent molecular ion in the mass spectrum was found at a molecular mass of m/e 294, and the base peak at m/e 249 corresponded to the fragment due to the loss of COOH . Other expected fragments due to loss of COOH , $\text{C}_6\text{H}_4\text{F}$, and $\text{COC}_6\text{H}_4\text{F}$, respectively, were also observed.

³⁶ F. W. Wehrli, A. P. Marchand and S. Wehrli, *Interpretation of Carbon-13 NMR Spectra*, 1988, 2nd Ed., 310.

Figure II.1. IR spectrum of 8-(4-fluorobenzoyl)-1-naphthoic acid.

II.3. Grignard Reaction with Acenaphthenequinone

Two keto groups in acenaphthenequinone enabled the double addition of the Grignard reagent in one step. A simple oxidation reaction of the resulting diol permitted the completion of the monomer synthesis in good yield.

II.3.1. Synthesis of 1,2-Dihydroxy-1,2-bis(4-fluorophenyl)acenaphthene

The Grignard reaction was run in a 1:2.5 molar ratio of acenaphthenequinone to organomagnesium reagent in THF (route c, Scheme II.1).³⁷ Acenaphthenequinone was added in small portions to a solution of 4-fluorophenylmagnesium bromide in THF, prepared from 1-bromo-4-fluorophenyl with magnesium turnings. The exothermic reaction was controlled by means of an ice bath. TLC showed the immediate consumption of the starting material and the formation of two products. After workup and recrystallization once from toluene, the diols were deemed sufficiently pure to be used in the following step without further purification. A small amount of the diols were further recrystallized for characterization.

The reported melting point was in the range 220-221 °C.³⁷ Instead, the measured melting point was 191-193 °C which means the presence of a mixture of cis and trans isomeric diols.³⁸ This fact is also confirmed by TLC analysis, showing the formation of two products. The presence of a mixture of isomers was evidenced in NMR by the more splitting for the protons on the phenyl ring. The assignment of the ¹H and ¹³C NMR chemical shifts are summarized in Tables II.1 and II.2, respectively. These assignments were supported by COSY and HETCOR experiments. The presence of a hydroxy peak and a clear coupling in the naphthalene ring in the ¹H NMR spectrum, plus the carbon-fluorine coupling for the phenyl unit and low shift quaternary carbon in the ¹³C NMR spectrum, clearly proved the structure of the diol.

³⁷ W. E. Bachmann and E. J. H. Chu, *J. Am. Chem. Soc.*, **1936**, *58*, 1118.

³⁸ T. Nonaka and M. Asai, *Bull. Chem. Soc. Jpn*, **1978**, *51* (10), 2976.

Table II.1. ^1H NMR results of 1,2-dihydroxy-1,2-bis(4-fluorophenyl)acenaphthene.

^1H NMR	H2	H3	H5	H7	H8	H9
δ	7.03	7.23	2.06	7.36	7.66	7.91
J, Hz	8.65 (2-3)	8.90 (2-3)	-	6.97 (7-8)	6.95 (7-8)	8.30 (8-9)
	8.65 (2-F)	5.38 (3-F)			8.28 (8-9)	

Table II.2. ^{13}C NMR results of 1,2-dihydroxy-1,2-bis(4-fluorophenyl)acenaphthene.

^{13}C	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11
δ	162.6	114.7	129.7	136.3	89.4	131.3	121.7	129.0	125.6	129.7	145.3
$ \Delta\text{C-F} $	247	21	9	-	-	-	-	-	-	-	-

The IR spectrum showed multiple peaks in the OH-stretching band region. Two sharp peaks at 3570 and 3510 cm^{-1} might be assigned to the trans isomer to account for free hydroxyl groups and intermolecular hydrogen bonding respectively. While the band at 3530 cm^{-1} could be assigned to intramolecular hydrogen bonding in the cis isomer.³⁸ MS showed the parent molecular ion at m/e 374 as expected and the base peak at m/e 249 corresponded to the fragment due to the loss of H_2O followed by $\text{C}_7\text{H}_4\text{F}$ radical. The fragmentation also showed the loss of $\text{COC}_6\text{H}_4\text{F}$. Thus the synthesis of the intermediate 1,2-dihydroxy-1,2-bis(4-fluorophenyl)acenaphthene was proved to be successful and the next step towards the synthesis of the monomer could be attempted.

II.3.2. Synthesis of 1,8-Bis(4-fluorobenzoyl)naphthalene

Chromic anhydride is a well-known oxidizing agent.^{39,40,41,42} Its oxidizing power increases with decreasing water content.³⁸ Therefore the oxidation is much faster and more efficient when done with a suspension of anhydrous chromic anhydride in glacial acetic acid which is also called the Fieser reagent.⁴⁰ Thus, the oxidation was effected with the Fieser reagent as attempted by Bachmann *et al.*³⁷ using as small amounts of reagents as possible.

Crude 1,2-dihydroxy-1,2-bis(4-fluorophenyl)acenaphthene was partially dissolved in 3 L of acetic acid. Chromic anhydride was then added to the suspension in small portions to control the exothermic reaction. The diol finally dissolved completely within a few minutes with darkening of the solution. The mixture was heated at 90 °C overnight . TLC showed the disappearance of two isomeric diols and the formation of a new product. The product was precipitated in cold water and recrystallized three times from toluene-methanol (1:1 v/v) as white crystals in overall 65% yield from acenaphthenequinone.

The ¹H and ¹³C NMR spectra (Figures II.2 and II.3) are consistent with the structure of desired monomer, as supported by COSY and HETCOR experiments. The chemical shifts and coupling constants are listed in Tables II.3 and II.4 .

³⁹ L. F. Fieser, *Reagents for organic synthesis*, 1967, I, 144.

⁴⁰ L. F. Fieser, *J. Am. Chem. Soc.*, 1948, 70, 3237.

⁴¹ L. F. Fieser and J. Szmuszkowicz, *J. Am. Chem. Soc.*, 1948, 70, 3352.

⁴² K. Nakanishi and L. F. Fieser, *J. Am. Chem. Soc.*, 1952, 74, 3910.

Figure II.2. ^1H NMR spectrum of 1,8-bis(4-fluorobenzoyl)naphthalene.

(400 MHz)

Figure II.3. ^{13}C NMR spectrum of 1,8-bis(4-fluorobenzoyl)naphthalene.
(100 MHz)

Table II.3. ^1H NMR data of 1,8-bis(4-fluorobenzoyl)naphthalene.

^1H NMR	H ₂	H ₃	H ₇	H ₈	H ₉
δ	7.07	7.87	7.54	7.54	8.02
J, Hz	8.64 (2-3)	8.69 (2-3)	-	-	8.75 (8-9)
	8.64 (2-F)	5.51 (3-F)			3.97 (7-9)
					3.97 (9-9')

Table II.4. ^{13}C NMR data of 1,8-bis(4-fluorobenzoyl)naphthalene.

^{13}C	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11
δ	165.7	115.3	133.0	134.0	196.3	136.7	129.7	132.1	125.0	128.7	135.0
$\text{C}-\text{F}$	255	22	9	3	-	-	-	-	-	-	-

The IR spectrum confirmed the presence of a carbonyl group (1665 cm^{-1}), and aromatic rings for peaks at 1593 and 1500 cm^{-1} . The MS spectrum showed a very simple fragmentation pattern with no parent molecular ion. The base peak was found at a mass of m/e 249 for the fragment due to the loss of $\text{COC}_6\text{H}_4\text{F}$ radical.

Thus, this two-step process yielded the monomer in fairly high yield and in high purity. With the highly pure monomer at hand the polymerizations were then carried out.

CHAPTER III. Naphthalene-based Poly(arylene ether ketone)s

III.1. Model Reaction

Scheme III.1. Model nucleophilic condensation.

In an attempt to test the reactivity of the monomer towards nucleophilic displacement reactions, a model reaction was performed. The monomer was reacted with two molar equivalents of phenol in $TMSO_2$ using potassium carbonate as a base (Scheme III.1). The azeotrope of the water formed and toluene was distilled off at 140 °C for two hours. The mixture was then reacted overnight at 180 °C. After precipitation in methanol, the solids were recrystallized twice from toluene-methanol (1:1 v/v) to afford 1,8-bis(4-phenoxybenzoyl)naphthalene as white crystals in high yield.

The 1H NMR spectrum of the product, as compared with the monomer, showed similar shifts for the proton in the naphthalene unit and the addition of the new phenyl ring was indicated by three new chemical shifts which clearly show couplings with each other. ^{13}C NMR confirmed the presence of the ketone and the fully aromatic structure of the product. 1H and ^{13}C NMR assignments for 1,8-bis(4-phenoxybenzoyl)naphthalene are listed in Tables III.1 and III.2, respectively.

Table III.1. ^1H NMR results of 1,8-bis(4-phenoxybenzoyl)naphthalene.

^1H	H ₂	H ₃	H ₇	H ₈	H ₉	H ₁₃	H ₁₄	H ₁₅
δ	6.90	7.78	7.55	7.55	8.03	7.07	7.38	7.17
J, Hz	9.0(2-3)	9.0(2-3)	-	-	7.5(8-9)	8.6	8.6	7.3
	2.2 met	2.1met			1.9(7-9)	(13-14)	(13-14)	(14-15)
						1.2	7.7	1.2
						(13-15)	(14-15)	(13-15)

Table III.2. ^{13}C NMR results of 1,8-bis(4-phenoxybenzoyl)naphthalene.

^{13}C	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	C ₈
δ	166.8	116.6	132.6	131.9	196.1	134.8	129.9	124.7
^{13}C	C ₉	C ₁₀	C ₁₁	C ₁₂	C ₁₃	C ₁₄	C ₁₅	
δ	131.6	128.7	136.9	155.2	129.5	120.3	124.5	

The IR spectrum, with absorption bands at 1649 cm^{-1} and 1244 cm^{-1} , confirmed the presence of the carbonyl and the ether link respectively. MS showed no parent molecular ion. The base peak was found at a mass m/e 323 corresponding to the fragment due to the loss of $\text{COC}_6\text{H}_4\text{OC}_6\text{H}_5$. The spectrum also indicated the possible loss of $\text{C}_6\text{H}_4\text{OC}_6\text{H}_5$ and OC_6H_5 radicals. Since the single product, 1,8-bis(4-phenoxybenzoyl)naphthalene, had been obtained in high yield, the monomer was proved reactive enough to form a polymer cleanly by nucleophilic displacement with a bisphenol.

III.2. Polymerization Reaction

Different reaction conditions were used to optimize the molecular weight of polymer, such as different solvents and reaction temperatures. In general, NMP, DMAc and TMSO₂ are common solvents for nucleophilic displacement polymerization. When polymerizations were carried out in TMSO₂ with chlorobenzene as an azeotroping agent at 230 °C, only low molecular weight polymers were formed, probably due to polymer degradation at elevated temperatures. It has been reported that the fluorine anion can cleave the ether bond in poly(arylene ether ketone) at high temperatures.⁴³ Thus, an azeotrope with a lower boiling co-solvent was needed to enable the polymerization run under mild conditions. Toluene was then used as an azeotroping agent. In DMAc a polymer did not form because of the insolubility of the monomer. High molecular weight polymers could be obtained in NMP but the polymer cleavage with potassium fluoride at elevated temperatures often occurred.²¹ Thus, polymerizations were carried out in TMSO₂ using a stoichiometric ratio of monomers in the presence of excess potassium carbonate (Scheme III.2). The resulting water was removed together with toluene at 140 °C during the initial stage of the polymerization. At the beginning of the polymerization, the solution concentration was kept high with about 45% solid contents. After complete dehydration (2 h) and raising the temperature to 180 °C, the reaction mixture became viscous and was diluted with TMSO₂ to ca. 25% solid contents. The progress of the polymerization was then monitored by running GPC of a small amount of samples, showing the increase of retention time (Figure III.1), e.g. increase in molecular weight, as the reaction progressed. The resulting polymers were isolated by precipitation into methanol, washed, and purified by reverse precipitation to remove all small amounts of oligomers.

⁴³ U. Hoffman, F. Helmer-Metzmann and K. Mullen, *Macromolecules*, 1994, 27, 3575.

Figure III.1. GPC traces of the formation of polymer III-2b.

Scheme III.2. Polymer synthesis.

The end-capping experiment (Figure III.1) was also performed in similar conditions in the presence of 3,5-di-tert-butylphenol. The reaction was carried out with a 1% excess of the difluoride and 2% of 3,5-di-tert-butylphenol relative to bisphenol III-1b. Polymer III-3 was expected to have the number of the repeat unit (n) of 100.⁴⁴

Figure III.2. End-capped polymer III-3

III.3. Characterization and Properties

All polymers appeared as white to off-white fibrous solids and displayed excellent solubility in chlorinated hydrocarbons, DMAc and NMP. Free-standing, transparent, tough films could be cast from chloroform or TCE.

⁴⁴ P. J. Flory, *Principles of Polymer Chemistry*, 1953, 91.

III.3.1. Spectroscopic Characterization

The NMR spectra of the polymers displayed the same basic pattern for the common naphthalene unit as the monomer or model compound. The results of ^1H and ^{13}C NMR for the polymer III-2c synthesized from hydroquinone are reported in Tables III.3 and III.4, respectively. Those assignments were supported by COSY and HETCOR experiments. The ^{13}C NMR spectrum of the polymer III-2c displayed 13 distinguishable lines for each of the different carbon atoms and matched well with that of structurally related 1,8-bis(4-phenoxybenzoyl)naphthalene that has two extra lines as expected (Figure III.3). A carbonyl peak was observed at 196 ppm for both.

III-2c

Table III.3. ^1H NMR results of polymer III-2c.

^1H NMR	H2	H3	H7	H8	H9	H13
δ	6.92	7.81	7.51	7.51	7.98	7.08
J, Hz	8.69 (2-3)	8.70 (2-3)	-	-	7.94 (8-9)	-

Table III.4. ^{13}C NMR results for polymer III-2c.

^{13}C	C1	C2	C3	C4	C5	C6	C7
δ	161.9	116.7	132.8	132.3	196.3	135.0	129.3
^{13}C	C8	C9	C10	C11	C12	C13	
δ	124.9	131.8	128.7	137.0	151.9	122.0	

Figure III.3. ^{13}C NMR spectra of polymer III-2c and 1,8-bis(4-phenoxybenzoyl)naphthalene.

The carbonyl absorption for these polymers in IR was found in the region of 1654-1661 cm^{-1} . The ether linkage was confirmed by a strong absorption in the region 1237-1247 cm^{-1} . These spectral data clearly indicated the formation of the expected polymers.

III.3.2. Molecular Weight

All of the important properties of a polymer, such as glass transition temperature (T_g) and thermal stability depend upon the polymer's molecular weight. In general, as the molecular weight increases, the physical properties improve until they reach a plateau value at which point, further increase in molecular weight will have only limited effect on the properties.

GPC in chloroform relative to polystyrene standards showed that high molecular weight products were obtained (Table III.5). The apparent weight average molecular weight for III-2a-f ranged from 58,700 to 213,000 g/mol. Relatively low molecular weight was obtained for the polymer synthesized from 1,4-hydroquinone. This might be accounted for the instability of the salts of hydroquinone formed during the polymerization. These salts are easily subject to oxidation.⁸ Thus the stoichiometry of the reactants is affected and the polymer with only low molecular weight is obtained. All GPC traces were monomodal with polydispersity factors (M_w/M_n) varying between 1.94 and 2.35.

Inherent viscosity gives an indication of the molecular weight of the polymer. In general, providing that the polymers with similar structures are being compared, the higher the viscosity, the higher the molecular weight. It is generally accepted that the polymers with aromatic structures of the type synthesized should at least have an inherent viscosity of 0.4 dL/g in order to have stable thermal properties. The high molecular mass of the polymers were evidenced by their inherent viscosities ranging from 0.45 to 0.78 dL/g in chloroform (Table III.5).

Table III.5. Molecular weight and inherent viscosities of the polymers III-2a-f.

Polymer III-2	Mw	Mn	Mw/Mn	η_{inh}^a
	$\times 10^{-4}$	$\times 10^{-4}$		(dL/g)
a	7.05	3.64	1.93	0.53
b	21.3	10.0	2.13	0.77
c	5.87	2.47	2.34	0.45
d	15.7	6.83	2.29	0.63
e	14.5	7.01	2.07	0.66
f	14.8	6.83	2.17	0.78

^a Measured in 0.5% chloroform solution at 25 °C.

The introduction of an end-capping agent during the polymerization permitted to control the molecular weight^{44,45} and also allowed the calculation of absolute number-average molecular weight or the number of repeat units. The calculation is based on the ratio of two peaks at 1.30 (t-butyl) and 8.02 ppm (H-*para* to carbonyl) in the ¹H NMR spectrum, which gives a number of the repeat units (n) in the polymer of 106 or a number-average molecular weight (Mn) of 70,800 g/mol. The apparent Mn was determined to be 52,700 g/mol by GPC, which is significantly less than the value calculated by NMR analysis. Therefore, the exact molecular weights of these polymers should be higher than the apparent ones determined by GPC.

III.3.3. Thermal Properties

None of these polymers showed any crystalline behavior as assessed by differential scanning calorimetry (DSC). The glass transition temperature (T_gs) were observed between 214 and 274 °C depending on the units derived from bisphenol monomers (Table III.6).

⁴⁵ T. Takeichi and J. K. Stille, *Macromolecules*, 1986, 19, 2108.

Figure III.4. DSC traces of polymers III-2a,c,d,f.

Polymer III-2d (Figure III.4) containing a bulky group has the highest Tg (274 °C) whereas others have Tgs all around 220 °C. As expected, the polymers with the lowest Tg are those prepared from BPA (III-1a) and 4,4'-(hexafluoroisopropylidene)diphenol (III-1b). These bisphenols contain no bulky groups but a flexible propylidene group. Intermediate Tgs were obtained for polymers prepared from 4,4'-diphenol and 1,4-hydroquinone, which are rigid but not bulky. Introducing a bulky, pendant tert-butyl group in the polymer prepared from 1,4-hydroquinone increased the Tg as demonstrated by the results of III-2c (Tg = 222 °C) and III-2f (Tg = 230 °C) (Figure III.4).

In general, introducing a rigid benzenoid into the polymer backbone is likely to increase the Tg. Polymer III-4 derived from BPA and 2,6-bis(4-fluorobenzoyl)naphthalene has the Tg of 185 °C, higher than that of analogue III-5 (160 °C)¹⁹ but very close to that of III-6 having the 4,4'-biphenylene unit (186 °C) (Table III.7).²² By comparing the structure feature in the repeat unit, polymer III-2a is less symmetric than III-4. But its Tg is actually 30 °C higher than that (Tg = 185 °C) of III-4. This noticeable increase in the Tg clearly demonstrates that two benzoyls at the 1,8-positions of naphthalene are in the fairly sterically congested environment similar to those in the 1,2-phenylenedicarboxyl and 2,2'-biphenylenedicarboxyl structures. Such a steric hindrance causes the increased restriction of free rotation of the bond connecting the naphthylene and the carbonyl groups and reduces the overall chain mobility. The similar effect is seen for polymer III-7 in which two methyl groups are in the *ortho* positions to the two carbonyl groups.

Table III.6. DSC and TG results for polymers III-2a-f

polymer III-2	T _g (°C) ^a	T _d (in N ₂) ^b	T _d (in air) ^b
a	215	475	480
b	214	526	522
c	223	529	522
d	274	534	529
e	228	537	533
f	230	475	478

^a Second scan at heating rate of 10 °C/min. ^b Temperature for 5% weight loss.

Table III.7. Comparisons of T_gs of structurally related polymers.

$\left[\text{O}-\text{C}_6\text{H}_4-\text{C}(\text{CH}_3)_2-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{Ar}-\text{C}(=\text{O})-\text{C}_6\text{H}_4 \right]_n$					
-Ar-
polymer	III-5	III-6	III-4	III-7	III-2a
T _g (°C)	160	186	185	222	215

The thermal and thermooxidative stabilities of the polymers were measured by thermogravimetry analysis (TG) in nitrogen and air, respectively (Table III.6). The 5% weight loss for the polymers III-2a-f ranged from 475 to 537 °C in nitrogen and 478 to 533 °C in air. Thus, the difference being negligible, the polymer decomposition can be concluded to occur in a similar way in both atmospheres. The thermal stability decreased

greatly in **III-2f** due to the presence of the weaker C-H bond in tert-butyl group as compared to polymer **III-2c** (Figure III.5). The weight losses were near 480 °C for **III-2f**, and above 520 °C for analogous **III-2c** without tert-butyl group. Polymer **III-2a** was also relatively less thermally stable, due to the presence of aliphatic methyl groups, than other wholly aromatic polymers **III-2c,d,e** and its fluorinated analogue **III-2b**. Nevertheless, in spite of their high Tgs, these poly(arylene ether ketone)s should be stable enough for melt processing.

Figure III.5. TG thermogram of polymers III-2a,c,d,f.

III.3.4. Mechanical Properties

The Young's moduli (E') of the polymers were obtained from thermomechanical analysis in the tensile stress-strain mode (Table III.8). The measurements were performed on thin strips of films cast from chloroform or TCE solution. The thin films of polymers were clear, creasable and tough. Loads were chosen such that linear stress-strain relationship was obtained. Two sets of Young's moduli were taken using different loads. With higher loads (offset = 20 g, Amp. = 10 g), higher E' were obtained. The high E' value (4.0 GPa) was observed for polymer III-2e due to the biphenylene unit in the repeat unit. High tensile moduli have been also reported for other biphenylene-containing poly(arylene ether ketone)s.^{22,46,47} The relatively low Young's modulus for III-2c may be due to residual TCE solvent in the film, different casting conditions or the low molecular weight of this polymer.

Table III.8. TMA results for polymers III-2a-e.

polymer III-2	T_g^a	E'^b (GPa)	E'^b (GPa)
	(max. $\tan \delta$)	load A	load B
a	206	0.60	0.70
b	212	1.75	2.17
c	182	0.82	0.96
d	268	1.20	1.70
e	225	1.60	4.40

^a $\tan \delta$ value, heating rate of 10 °C/min. ^b Young's modulus at 25 °C; load A: offset = 10 g, Amp. = 5 g; load B: offset = 20 g, Amp. = 10 g.

⁴⁶ P. Moulinie, R. Paroli and Z. Y. Wang, *J. Polym. Sci., Polym. Chem.*, submitted in 1994.

⁴⁷ P. A. Clendinning, M. J. El-Hibri, M. Matzner and G. T. Kwiatkowski, *Polym. Preprints*, 1991, 32(2), 166.

As the temperature is increased, the modulus will remain high until the glass transition temperature is reached, at which point the modulus drops sharply. Thus, The Tg could also be measured by TMA as a maximum value of $\tan \delta$ peak (Table III.8). When compared to the results obtained by DSC (Table III.6), polymers III-2a,b,d,e showed very little difference in Tgs. Polymer III-2c had the lowest molecular weight among all polymers synthesized and was cast from TCE instead of chloroform. Its Tg was found much lower (40 °C difference) by TMA than by DSC, which means that the different casting conditions or lower molecular weight can infer on the TMA results.

CHAPTER IV. Acenaphthylene-based Polymers

IV.1. Precursor Strategy in Polymer Synthesis

The increase in rigidity or chain stiffness of a polymer backbone usually leads to increased solvent resistance and improved thermal properties, e.g., higher T_g and oxidative stability. But the direct synthesis of rigid polymers is usually hampered by the poor solubility of the growing polymers and the lack of suitable reactive monomers, leading to the precipitation of oligomers or ill-defined materials. Therefore, new synthetic approaches had to be developed. The precursor strategy involves a stepwise procedure involving the synthesis of soluble polymeric material by a well-known polycondensation and the generation of the final structure by a subsequent polymer transformation reaction. The resultant solubility of the precursor facilitates the synthesis, allowing higher molecular weights to be achieved. Within this strategy, a number of different approaches were studied.

The introduction of side chain on the polymer backbone is known to increase the solubility of the resulting polymer. Removal of the side group then generates the target polymer in high molecular weight.⁴⁸ The *tert*-butyl group has been used to enhance the solubility of the precursor PEEK and is readily removed by the acid-catalyzed trans-*tert*-butylation to yield PEEK.⁴⁹ High molecular weight, insoluble poly(p-phenylene) has also been synthesized by the thermolysis of soluble, high molecular weight precursor polymer (Scheme IV.1).⁵⁰

⁴⁸ A. Noll, N. Siegfried and W. Heitz, *Makromol. Chem., Rapid Commun.*, **1990**, *11*, 485.

⁴⁹ W. Risse and D. Y. Sogah, *Polym. Preprints*, **1990**, *31* (1), 616.

⁵⁰ D. L. Gin, V. P. Conticello and R. H. Grubbs, *J. Am. Chem. Soc.*, **1992**, *114*, 3167.

Scheme IV.1. High molecular weight poly(p-phenylene) from soluble precursor polymer.

Another approach involves using protecting groups in starting monomers. The protecting group acts as the pendant group which imparts solubility, and at the same time retains the reactivity of the monomer. The synthesis of polyketones, which are known as highly crystalline polymers, was effected through the polymerization of amorphous poly(aminonitrile sulfone)s. The carbonyl moieties were then regenerated by acid treatment in the final step.⁵¹ Semicrystalline PEEK has also been prepared from soluble precursor poly(arylene ether ketimine) by the hydrolysis of the ketimine (Scheme IV.2).⁵²

Scheme IV.2. PEEK from soluble ketimine precursor.

⁵¹ H. W. Gibson, J. Wang and A. Pandya, *Polym. Preprints*, 1993, 43 (1), 570.

⁵² B. E. Lindfors, R. S. Mani, J. E. Mc Grath and D. K. Mohanty, *Makromol. Chem., Rapid Commun.*, 1991, 12, 337.

The last approach, and also the most widely used one, involves the formation of suitably functionalized open-chain precursors and subsequent ring-closure upon thermal, chemical or light treatment. A typical example is the introduction of an anthracene ring into poly(phenylquinoxalines) by thermal intramolecular cyclization of pendant acetylene groups which results in increased creep and craze resistance and higher glass transition temperatures (Scheme IV.3).⁵³ But further requirements for this type of reaction include the need for quantitative conversion of the open-chain starting material and high chemo- and regioselectivity in the reaction to minimize structural effects like cross-links.

Scheme IV.3. Cyclization of pendant acetylene groups in poly(phenylquinoxalines).

Thus, the final structure must be predetermined in its precursor such that the actual intramolecular ring-closure reaction is greatly favored over all possible side reactions, e.g., intermolecular couplings. For example, the intramolecular cyclization of poly(arylene ether

⁵³ P. M. Lindley and B. A. Reinhardt, *J. Polym. Sci. Polym. Chem.*, 1991, 29, 1061.

ketone)s having 2,2'-dibenzoylbiphenyl units resulted in the formation of non-cross-linked, phenanthrene-based poly(arylene ether)s (Scheme IV.4). The transformation of the polymer induced an increase in the T_g and the thermal stability as expected from the increased rigidity of the polymer backbone.⁵⁴

Scheme IV.4. Intramolecular deoxy-olefination reaction.

Since the formation of a phenanthrene ring from a flexible 2,2'-diacylbiphenyl was proved via a dithioketone intermediate⁵⁵ and was successfully applied to polymer chemistry,⁵⁶ the formation of acenaphthylene ring from 1,8-diacylnaphthalene should proceed in a similar way. Thus, poly(arylene ether ketone)s III-2a-f would also be useful as precursor polymers for acenaphthylene-containing poly(arylene ether)s.

⁵⁴ C. Zhang and Z. Y. Wang, *Macromolecules*, 1993, 26, 3330.

⁵⁵ K. Steliou, P. Salama and X. Yu, *J. Am. Chem. Soc.*, 1992, 114, 1456.

⁵⁶ Z. Y. Wang and C. Zhang, *Macromolecules*, 1992, 25, 5851.

IV.2. Model Compound

Scheme IV.5. Model cyclization reaction.

A model reaction was first carried out using the starting monomer, 1,8-bis(4-fluorobenzoyl)naphthalene, in order to confirm the feasibility of the polymer transformation (Scheme IV.5). A number of thionating agents, such as Lawesson's reagent,⁵⁷ phosphorus pentasulfide,^{58,59} and B₂S₃ generated in situ from BCl₃ and tricyclohexyltin sulfide,⁵⁵ can be used to effect the cyclization. Lawesson's reagent, though very efficient for the polymer transformation,⁵⁶ was found to yield by-products making the purification difficult. The main advantages of using phosphorus pentasulfide are the good yields obtained, no formation of organic by-products and a facile purification of the final products.⁶⁰ Thus, phosphorus pentasulfide was added slowly to 1,8-bis(4-fluorobenzoyl)naphthalene in pyridine. The reaction mixture was then heated up to 90 °C for 3 hours. The solution turned from light yellow to blue-green, indicating the formation of the corresponding thioketone and finally to dark-red, corresponding to the formation of the acenaphthylene unit. TLC also indicated the consumption of the starting material. The solution was then concentrated and quenched with HCl to destroy the remaining phosphorus pentasulfide. H₂S evolved was trapped in two successive traps containing NaOH and KMnO₄, respectively. The remaining sulfur by-products were removed by complexing with CuSO₄ as black solids of CuS. Recrystallization twice from toluene

⁵⁷ M. I. Thomsen, K. Clausen, S. Scheibye and S.-O. Lawesson, *Organic Syntheses*, 1984, 62, 158.

⁵⁸ G. W. Kirby and W. M. McGregor, *J. Chem. Soc., Perkin Trans 1*, 1990, 3175.

⁵⁹ J. W. Greidanus, *Can. J. Chem.*, 1970, 48, 3530.

⁶⁰ W. M. McGregor and D. C. Sherrington, *Chem. Soc. Reviews*, No 19, 202.

yielded 7,8-bis(4-fluorophenyl)acenaphthylene as orange solids. The solids melted in the range of 157-159 °C.

The purity of the product formed was confirmed by NMR. The results of ^1H and ^{13}C NMR were supported by COSY and HETCOR experiments (Tables IV.1 and IV.2, respectively). The ^{13}C NMR spectrum showed the disappearance of the carbonyl peak and the appearance of a new peak in the aromatic region belonging to a quaternary carbon.

Table IV.1. ^1H NMR results for 7,8-bis(4-fluorophenyl)acenaphthylene.

^1H	2	3	7	8	9
δ	7.07	7.39	7.70	7.61	7.88
J, Hz	8.7 (2-3)	8.8 (2-3)	6.9 (7-8)	7.0 (7-8)	8.1 (8-9)
	8.7 (2-F)	5.8 (3-F)		8.1 (8-9)	

Table IV.2. ^{13}C NMR results for 7,8-bis(4-fluorophenyl)acenaphthylene.

^{13}C	1	2	3	4	5	6	7	8	9	10	11
δ	162.2	115.6	131.6	131.0	128.1	137.2	123.9	127.6	127.9	128.5	139.7
$ \text{C}-\text{F} $	247	21.4	7.9	3.4	-	-	-	-	-	-	-

IR also showed the disappearance of the ketone peak, and the appearance of peaks in 1400-1600 cm^{-1} range accounted for aromatic double bonds. MS showed a very simple spectrum with a strong parent molecular ion at m/e 340 and no major fragment loss. UV-VIS spectrum displayed major absorption peaks at 240 and 335 nm, and a weak shoulder around 425 nm. Thus, those results proved that the cyclization had well been effected and that this reaction could be attempted on the polymer.

IV.3. Polymer Transformation

Lawesson's reagent was found to be a suitable thionating agent for the cyclization of the polymer due to the easy purification of the polymer compared to model compound. Polymers **III-2a-f** were simply treated with Lawesson's reagent in TCE.

Scheme IV.6. Polymer transformation.

As a typical procedure, the polymer was dissolved in TCE. Lawesson's reagent was added and the temperature was raised to 110 °C. As Lawesson's reagent began to dissolve, the polymer reacted as evidenced by the change in color from light yellow to dark purple and finally to light orange. IR spectra were taken from polymer samples to follow the polymer transformation. After 2 hours at 110 °C, the reaction was stopped. Vacuum distillation and precipitation into methanol resulted in an orange powder which was further purified by washing with methanol in a Soxhlet extractor. Further drying yielded polymers **IV-1a-f** as powders in good yields. The polymers were all insoluble in common solvents, forming gel-like products. The gel formation is usually characteristic of crosslinking. In the

presence of a solvent, a cross-linked polymer swells as the solvent molecules penetrate the network. Considering that the intramolecular reaction is favored in diluted reaction medium, other reaction conditions were used in order to compare the results.

The reaction was also attempted in more dilute solutions, following the same method as described previously. The reaction was followed by IR and a longer reaction time was required due to the lower concentration of reagents. Two days were usually needed for completion under these conditions. After usual workup, another series of polymers IV-2a-f that are similar to IV-1a-f were obtained. Most of IV-2a-f were found to be soluble in TCE and chloroform. Only the cyclization of polymer III-2c derived from hydroquinone did not yield the soluble polymer.

IV.4. Characterization and Properties

All polymers appeared as orange-brown to deep-orange powders. Polymers IV-1a-f were insoluble and formed gels in solution. Polymers IV-2a,b,d,e were soluble in chloroform and TCE. However, all polymers were tested positive for sulfur.⁶¹

IV.4.1. Spectroscopic Characterization

NMR analyses of soluble polymers IV-2a,b,d,e were attempted but broad lines in the spectra did not enable a specific interpretation. This line broadening could be explained by the increased rigidity of the polymer backbone which would hamper the relaxation of the nuclei.

Due to their insolubility, polymers IV-1a-f were characterized by IR. The spectra showed peaks in the regions of 1488-1499 and 1222-1240 cm^{-1} accounting for aromatic double bonds and ether linkage, respectively. No evidence of the presence of sulfur could be obtained from the IR spectra. This can be explained by the fact that C-S and S-S stretch

⁶¹ B. S. Furniss, A. J. Hannaford, P. W. Smith and A. R. Tatchell, *Vogel's textbook of practical organic chemistry*, 1989, 5th Ed., 1207.

bands are weak contrary to S=O or SO₂ bands which are strong in the IR.⁶² UV-VIS spectra for polymers IV-2a,b,d,e displayed similar peaks (at 338,430 nm) as for 7,8-bis(4-fluorophenyl)acenaphthylene, proving that a substantial amount of acenaphthylene unit had been formed.

IV.4.2. Molecular Weight

Again because of the insolubility, polymers IV-1a-f could not be characterized by GPC and viscosity measurements. For soluble polymers IV-2a,b,d,e, GPC (Table IV.3) showed higher retention times or lower apparent molecular weights than those of their parent polymers III-2a,b,d,e. The apparent weight-average molecular weights for IV-2a,b,d,e ranged from 31,500 to 60,200 g/mol. The polymers also showed a dramatic decrease in inherent viscosity (Table IV.3), ranging between 0.19 and 0.23 dLg⁻¹. The decreases in apparent molecular weight and viscosity can be accounted for the decreased linearity of the polymer backbone, which is also an indication of the formation of the acenaphthylene rings that should push the polymer chain into the U-turn shape.

Table IV.3. Molecular weights and inherent viscosities of polymers IV-2a,b,d,e.

polymer IV-2	Mw x 10 ⁻⁴	Mn x 10 ⁻⁴	Mw/Mn	η_{inh} (dL/g)
a	5.0	2.2	2.27	0.21
b	6.0	2.8	2.15	0.23
d	3.1	1.4	2.25	0.19
e	5.3	2.5	2.12	0.23

⁶² D. Lin-Vien, N. B. Colthup, W. G. Fateley and J. G. Grasselli, *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*, 1991, 225.

IV.4.3. Thermal Properties

For polymers IV-1a-f, none of them showed any T_gs as assessed by DSC. The first scan showed the appearance of two consecutive peaks, one exotherm followed by an endotherm (Table IV.4). As an example, DSC traces of two scans of polymer IV-1a is shown in Figure IV.1. The exotherm usually indicates the crystallization, ring-opening, rearrangement or stable bond formation taking place. The second scan showed no noticeable peak. Thus the process occurring in the first scan is irreversible. The exothermic peak was observed for all polymers in the same temperature range (230-250 °C), indicating that the bisphenol moiety in the polymer did not take part in any rearrangement or other reactions. Otherwise, the exotherm should occur at different temperatures because of the structural difference in those bisphenols.

Figure IV.1. DSC traces of polymer IV-1a.

TG thermogram showed two different weight losses at different temperatures for all polymers (Table IV.4) . The diagrams and weight loss temperatures were similar in both air and nitrogen, thus both decompositions occurred in the same manner. The first weight loss occurred between 246 and 272 °C, corresponding with the endothermic peak observed by DSC. The second weight loss was found in the range 459 to 565 °C, corresponding to usual thermal degradation, as shown in Figure IV.2 for polymers IV-1a,c,d,f. In comparison with parent polymers III-2a-f, polymers IV-1a-f were slightly more stable as expected from the added benzenoid in the polymer backbone. The thermal stability decreased greatly in IV-1a,f due to the presence of weaker C-H bonds in methyl and tert-butyl groups, respectively.

TG-IR was run on polymer IV-1d, in air. Gaseous SO₂ was detected by IR at temperatures between 240-280 °C for the first weight loss in TG (Figure IV.4). Thus, the first weight loss must be due to the elimination of sulfur from the polymer backbone, which then is oxidized with the oxygen in air to form SO₂.

Figure IV.2. TG thermograms of polymers IV-1a,c,d,f.

Table IV.4. DSC and TG results for polymers IV-1a-f.

polymer	exotherm	endotherm	Td ₁ ^b	Td ₁ ^b	Td ₂ ^c	Td ₂ ^c
IV-1	(max) ^a	(min) ^a	(in N ₂)	(in air)	(in N ₂)	(in air)
a	244.7	281.9	261.1	259.0	502.0	496.2
b	241.7	283.0	246.4	240.4	534.2	533.4
c	230.4	276.9	253.1	246.4	538.2	539.2
d	250.4	310.6	268.6	260.4	541.3	537.6
e	244.9	294.4	271.9	272.7	565.1	563.4
f	234.7	286.4	258.5	256.5	458.7	477.2

^a Determined by DSC at a heating rate of 10 °C/min. ^b Onset temperature for the first weight loss by TG at a heating rate of 20 °C/min ^c Onset temperature for the second weight loss in TG.

For soluble polymers IV-2a,b,d,e, again, no Tgs were observed on the DSC curves (Figure IV.3). The diagrams showed different patterns depending on the polymer (Table IV.5). Polymer IV-2a showed an exothermic peak around 209 °C but no endotherm. Polymers IV-2b and 2d both showed exotherm and endotherm peaks in the same temperature range as polymers IV-1. Finally, polymer IV-2d showed no peak. The second scan of all polymers showed no noticeable peak.

TG gave similar results as for polymers IV-1 (Table IV.5). The first weight loss occurred in the same temperature range (255-277 °C) but the second weight loss was usually observed at lower temperatures (379-546 °C). TG-IR of polymer IV-2d in air also proved the loss of SO₂ or the presence of sulfur. IR spectra of the volatiles from polymers IV-1d and IV-2d at 310 and 340 °C, respectively, match well with that of authentic SO₂ (Figure IV.4).

Figure IV.3. DSC traces of polymers IV-2a,b,d,e.

Figure IV.4. IR spectra of polymers IV-1d, IV-2d, and SO₂.

Table IV.5 DSC and TG results of polymers IV-2a,b,d,e.

polymer IV-2	exotherm ^a	endotherm ^a	Td ₁ ^b	Td ₂ ^c
	(max)	(min)	(in N ₂)	(in N ₂)
a	209.2	.d	255.1	379.0
b	241.2	284.5	262.5	515.7
d	.d	.d	277.5	521.9
e	240.9	271.5	258.3	546.0

^a Determined by DSC at a heating rate of 10 °C/min ^b Onset temperature for the first weight loss by TG at a heating rate of 20 °C/min ^c Onset temperature for the second weight loss in TG ^d Not observed.

The characteristic behavior of polymers IV-1a-f in solution, showing gel formation, led to the conclusion that these polymers were cross-linked. No structural evidence could be obtained to indicate the type of cross-linking bond due to the insolubility of the polymers. IR showed no unusual peak which can be explained by the fact that C-S bonds only displays very weak peaks in IR. DSC showed the occurrence of the elimination of sulfur at relatively low temperatures. The presence of sulfur in the polymer was confirmed by TG-IR. Therefore, polymers IV-1a-f are believed to be cross-linked by sulfur.

Because of their good solubilities in organic solvents, polymers IV-2 are not believed to be cross-linked. Their UV spectra displayed the characteristic pattern of acenaphthylene. However, DSC and TG still showed similar traces as polymers IV-1. TG-IR also demonstrated the loss of SO₂. Thus, even though polymers IV-2 are linear or non-cross-linked, they still contain sulfur. This means that the sulfur is only partially eliminated or the formation of the acenaphthylene ring is incomplete.

Scheme IV.7. Possible pathways to linear and cross-linked polymers.

On the basis of the results obtained, the 5-membered cyclization for acenaphthylene seems not as efficient as the 6-membered one for phenanthrene (Scheme IV.4). Both inter- and intramolecular coupling reactions can occur for the acenaphthylene system. The reaction tends to lead to crosslinking at high solution concentrations. As shown in Scheme IV.7, a possible pathway, as suggested by Steliou for the model compounds,⁵⁵ for the enthalpically-favored transformation of the ketone polymer to the acenaphthylene polymer involves the 1,2-dithietane intermediate **B** generated from the dithioketone **A** and the intramolecular formation of a carbon-carbon double bond upon extrusion of the diatomic sulfur. An intermolecular dimerization of **A** would lead to the formation of the cross-linked disulfide **C** which could extrude sulfur to yield the cross-linked sulfide **D**. Alternatively, **C** could be formed directly from the dithioketone **A** or by reaction of the extruded sulfur with the newly formed acenaphthylene at its reactive double bond. The later reaction is known as the vulcanization of elastomers containing double bonds.^{63,64} Many types of cross-linking bonds can exist in polymers IV-1, but none of them has been confirmed yet. Since

⁶³ G. Odian, *Principles of Polymerization*, 1991, 3rd Ed, 701.

⁶⁴ R. J. Young and P. A. Lovell, *Introduction to polymers*, 1991, 2nd Ed., 301.

polymers **IV-2** are quite soluble and also contain sulfur, they likely have some acenaphthylene rings and some cyclic 1,2-dithietane units like **B** or unreacted thioketones **A**.

CONTRIBUTION TO KNOWLEDGE

- **Monomer:** synthesized by Grignard reaction on acenaphthenequinone followed by oxidation of the diol formed. 1,8-Bis(4-fluorobenzoyl)naphthalene was obtained in high yield after purification by recrystallization.

- **Polymer synthesis:** nucleophilic displacement reaction of the monomer with a variety of bisphenols using potassium carbonate as a base and TMSO₂ as a solvent. Water formed during the reaction was distilled off as an azeotrope with toluene. Gel permeation chromatography and viscosity measurements proved the high molecular weights of the polymers synthesized. Absolute molecular weight of an end-capped polymer resulted in higher molecular weights than the GPC results.

- **Polymer properties:** T_{gs}, measured by differential scanning calorimetry, ranged from 214 to 274 °C. The 5 % weight losses of the polymers by thermogravimetry occurred all above 476 °C in nitrogen and 478 °C in air. Thermomechanical analysis showed good resistance of the polymers to tensile stress.

- **Polymer transformation:** intramolecular cyclization of the naphthalene-based poly(arylene ether ketone)s into acenaphthylene-based poly(ether ketone) by reaction with Lawesson's reagent could not be successfully effected. The deoxy-olefination run at either low or high concentration resulted in the formation of non-cross-linked and cross-linked polymers, respectively. Sulfur was proved to be still present in the cyclized polymers and induced a weight loss at low temperatures as seen by DSC and TGA. Possible synthetic pathways were proposed but the polymer structures could not be detailed.

EXPERIMENTAL SECTION

MATERIALS

1-Bromo-4-fluorobenzene, acenaphthenequinone, 2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide (Lawesson's reagent), 3,5-di-*tert*-butylphenol, 1,1,2,2-tetrachloroethane (TCE), *N*-methyl-2-pyrrolidinone (NMP), tetramethylenesulfone (TMSO₂), chlorobenzene, pyridine, fluorobenzene, aluminum chloride and other common organic solvents were purchased from Aldrich Chemical Co. and used as received. Tetrahydrofuran (THF, Aldrich) was dried by refluxing over sodium wire prior to use. 4,4'-Isopropylidenediphenol (BPA, Aldrich), 4,4'-(hexafluoroisopropylidene)diphenol (Aldrich), 9,9-bis(4-hydroxyphenyl)fluorene (General Electric Co.) were recrystallized from toluene, 4,4'-diphenol (Aldrich), and 1,4-hydroquinone (Aldrich) were purified by recrystallization from ethanol. *Tert*-butyl-1,4-hydroquinone (Aldrich) was purified by sublimation.

CHARACTERIZATION

Melting points were taken on a Fischer-Johns melting point apparatus and are uncorrected. Infrared measurements were performed on a Bomem-FTIR Michelson series instrument with a resolution of 4 cm⁻¹, the spectrum were recorded after 5 scans. The ¹H and ¹³C NMR spectra were recorded in chloroform-*d* solutions on either a Varian Gemini-200 or a Bruker-400 instruments and results are reported in ppm from tetramethylsilane on the δ scale. The coupling constants were assigned by assuming first order spectrum were obtained. Low resolution mass spectra were obtained on a Du Pont 21-492B spectrometer. Molecular weights were determined relative to polystyrene standards using chloroform as an eluent at the flow rate of 1.0 mL per min on a Perkin Elmer LC-250 GPC equipped with a PL gel column (5 μ m) and a UV detector set at 254 nm wavelength. Inherent viscosity data were obtained with a Ubbelohde viscometer (size OB114) in 0.5% (g/dL) chloroform

solution at 25 °C. The glass transition temperatures (T_g s) of the polymers were obtained using a Seiko 220C DSC instrument at a heating rate of 10 °C/min in N₂ (50 mL/min). The T_g values were reported from the second scan, otherwise as indicated. The T_g was taken from the midpoint of the change in the slope of the baseline. The weight loss data were obtained from a Seiko 220 TG/DTA instrument at a heating rate of 20 °C/min under either N₂ or air (200 mL/min). For all DSC and TG measurements, polymer pellets were lightly pressed, and a sample of 8-12 mg was used for each measurement.

FILM CASTING

Polymer films were cast from chloroform or TCE. A typical procedure is as follows: a polymer (150 mg) was dissolved in 2 mL of solvent. This solution was filtered and transferred into a glass ring (diameter = 6.5 cm, height = 2 cm, thickness = 0.2 cm) placed on a glass plate. The glass ring was covered with a glass plate and the solvent was allowed to slowly evaporate at room temperature over 24 h. The resulting tough and flexible films were further dried in a vacuum oven. The oven temperature was gradually increased from 50 to 200 °C over a period of 2 days. The film thickness ranged from 0.060 to 0.090 mm.

MEASUREMENT OF MECHANICAL PROPERTIES

A typical procedure to obtain Young's Modulus measurements was performed as follows: a stamp was used to cut out a film strip (length = 5 mm, width = 2 mm, thickness = 0.07 mm) which was mounted between two chucks in a Seiko TMA/SS 120 instrument. For Young's modulus at 25 °C, the parameters were set as: offset load = 10-20 g, load amplitude = 5-10 g and cycling frequency = 0.05 Hz. After this data was collected for 30 min., the same film was used without changing the parameters to measure Young's modulus (E') variation with temperature by heating to a temperature 40 °C higher than the T_g of the polymer studied at a ramp rate of 3 °C/min in static air.

MONOMER SYNTHESIS

8-(4-Fluorobenzoyl)-1-naphthoic acid.

Method A: In a 250 mL flask fitted with a reflux condenser, a thermometer and a nitrogen inlet, 1,8-naphthalic anhydride (2.50 g, 12.6 mmol) and fluorobenzene in excess (97 mL, 1035 mmol) were stirred under nitrogen for 15 min. The solution was heated up to 80 °C in order to dissolve the anhydride without success. After cooling down to 50 °C, AlCl_3 (4.30 g, 32.2 mmol) was carefully added to the mixture. The temperature of the solution raised slightly and the color changed from light yellow to brown. The mixture was then heated up to reflux. Nitrobenzene (2 mL) was added to dissolve the remaining solids, and the color then turned dark green. The mixture was allowed to react for one day. TLC analysis (ethyl acetate/ hexane, 40/60) showed no consumption of the starting material so the reaction was stopped without further analysis.

Method B: 1,8-Naphthalic anhydride (25.0 g, 126 mmol) and dry THF (150 mL) were charged in a 250 mL flask fitted with a reflux condenser and a nitrogen provider. 4-Fluorophenylmagnesium bromide (1 M solution in THF, 130 mL, 130 mmol) was slowly added dropwise to a well-stirred suspension over a period of 2 hours. TLC analysis (CHCl_3) showed the immediate consumption of the starting material but the mixture was allowed to react for another hour. The product was then hydrolyzed upon addition of ice (100 g). The mixture of hydrolyzed product was poured into a beaker containing dilute HCl (20%, 200 mL). The solution was extracted with chloroform (3x100 mL). The organic phase was then extracted with a solution of aqueous NaOH (1 M, 2x100 mL). The aqueous phase was treated with HCl, precipitating white solids. The solids were filtered and recrystallized from toluene, yielding white crystals of 8-(4-fluorobenzoyl)-1-naphthoic acid: 27.9 g (75%); mp 156-158 °C; IR (KBr, cm^{-1}) 3303 (O-H), 1682 (C=O); MS (m/e , relative intensity) 249 ($\text{M}^{+}-\text{CO}_2\text{H}$, 100).

1,2-Dihydroxy-1,2-bis(4-fluorophenyl)acenaphthene.

In a flame dried 1 L round-bottomed flask fitted with a mechanical stirrer, a reflux condenser and a nitrogen provider was placed dry magnesium turnings (33.0 g, 1.40 mol). To the flask were added THF (100 ml) and 1-bromo-4-fluorobenzene (15.0 mL, 0.13 mol). The mixture was heated slowly up to reflux under nitrogen. The appearance of a brown coloration around the magnesium turnings indicated the beginning of the reaction forming the Grignard reagent. The stirring was turned on and the rest of THF (400 mL) and 1-bromo-4-fluorobenzene (128 mL, 1.12 mol) were added dropwise. At the end of the addition, the mixture was stirred at room temperature for another hour. The mixture was diluted with 250 mL of THF. Acenaphthenequinone (95.0 g, 0.52 mol) was then added in small portions over 1 hour. The exothermic reaction was controlled by means of an ice bath. After one hour of reaction, TLC analysis (ethyl acetate/ hexane, 40/60) showed the consumption of the starting material. Ice (300 g) was added in the reaction flask to hydrolyze the magnesium salt. The mixture of hydrolyzed product was then poured into a beaker containing aqueous acetic acid (10%, 1 L), resulting in the precipitation of white solids. The solids were filtered and recrystallized from toluene once. A small amount of the solids was further purified to characterize 1,2-dihydroxy-1,2-bis(4-fluorophenyl)acenaphthene: mp 191-193 °C (lit. mp 220-221 °C, 153.5-154.5 °C³⁷); IR (KBr, cm⁻¹) 3570, 3510 (O-H); ¹H NMR (400 MHz) 7.91 (d, 2 H, J_{H-H} = 8.30 Hz), 7.66 (d d, 2 H, J_{H-H} = 8.28 Hz, J_{H-H} = 6.95 Hz), 7.36 (d, 2 H, J_{H-H} = 6.97 Hz), 7.23 (m, 4 H), 7.03 (t, 4 H, J_{H-H} = J_{H-F} = 8.65 Hz), 2.06 (s, 2 H); ¹³C NMR (100 MHz) 163.86, 161.40 (J_{C-F} = 247.2 Hz), 145.32, 136.27, 131.26, 129.73, 129.65 (J_{C-F} = 8.9 Hz), 129.01, 125.63, 121.71, 114.85, 114.64 (J_{C-F} = 21.1 Hz), 89.42; MS (m/e, relative intensity) 249 (M⁺ - ·COPhH₂F, 100).

1,8-Bis(4-fluorobenzoyl)naphthalene.

After filtration, the solids of 1,2-dihydroxy-1,2-bis(4-fluorophenyl)acenaphthene were mixed with CrO_3 (80.0 g, 0.53 mol) in 3 L of acetic acid in a beaker. The mixture was heated up until all solids dissolved and held at 90 °C overnight. TLC analysis (ethyl acetate/ hexane, 40/60) showed the consumption of the diol. After cooling to room temperature, the solids were precipitated out upon addition to cold water. After filtration and rinsing with hot water, the product was recrystallized three times from toluene-methanol (1:1 v/v) to yield white crystals: 122.0 g (65%); mp 166.0-168.0 °C (lit. mp 166.5-167.5 °C³⁷); IR (KBr, cm^{-1}) 1665 (C=O); ^1H NMR (400 MHz) 8.07 (m, 2 H), 7.87 (d d, 4 H, $J_{\text{H-H}} = 8.69$ Hz, $J_{\text{H-F}} = 5.51$ Hz), 7.54 (m, 4 H), 7.07 (t, 4 H, $J_{\text{H-H}} = J_{\text{H-F}} = 8.64$ Hz); ^{13}C NMR (100 MHz) 196.30, 166.98, 164.45 ($J_{\text{C-F}} = 254.8$ Hz), 136.68, 135.01, 134.03, 134.00 ($J_{\text{C-F}} = 2.9$ Hz), 133.05, 132.96 ($J_{\text{C-F}} = 9.4$ Hz), 132.08, 129.73, 124.98, 115.46, 115.24 ($J_{\text{C-F}} = 21.9$ Hz); MS (m/e, relative intensity) 249 ($\text{M}^+ - \cdot\text{COPhF}$, 100).

MONOMER TRANSFORMATION

7,8-Bis(4-fluorophenyl)acenaphthylene.

In a 250 mL round-bottomed flask fitted with a reflux condenser and a nitrogen provider, were placed 1,8-bis(4-fluorobenzoyl)naphthalene (20.0 g, 54 mmol) and pyridine (150 mL). To the resulting solution was added phosphorus pentasulfide (9.1 g, 41 mmol) in small portions over 10 min and the reaction mixture was heated up to 90 °C. The solution turned from light yellow to blue-green and finally to dark red after 1 hour of reaction. After 3 hours of reflux, TLC analysis (ethyl acetate/ hexane, 40/60) indicated the consumption of the starting material. The solution was concentrated to 50 mL by vacuum distillation. The reflux condenser was then fitted with a succession of two traps, the first one containing NaOH (40%, 100 mL), and the second one filled with a solution of basic KMnO_4 to trap H_2S evolved in the next step. Dilute HCl (10%, 150 mL) placed in a

dropping funnel was then carefully added to destroy the remaining phosphorus pentasulfide. CuSO_4 powder was added to the mixture in a beaker, precipitating dark solids. The mixture was extracted twice with diethyl ether (100 mL). The ethereal phase was washed twice with dilute HCl (10%, 50 mL), twice with water (50 mL), once with brine (50 mL), and then dried over Na_2SO_4 . Evaporation of solvent afforded orange solids which were recrystallized twice from toluene to yield 7,8-bis(4-fluorophenyl)acenaphthylene: 10.5 g (57%); mp 157.0-159.0 °C; IR (KBr, cm^{-1}) 3040 ($=\text{C-H}$), 1217 (C-O-C); ^1H NMR (400 MHz) 7.88 (d, 2 H, $J_{\text{H-H}} = 8.12$ Hz), 7.70 (d, 2 H, $J_{\text{H-H}} = 6.94$ Hz), 7.61 (d d, 2 H, $J_{\text{H-H}} = 7.02$ Hz, $J_{\text{H-H}} = 8.14$ Hz), 7.39 (d d, 4 H, $J_{\text{H-H}} = 8.83$ Hz, $J_{\text{H-F}} = 5.83$ Hz), 7.07 (t, 4 H, $J_{\text{H-H}} = 8.73$ Hz); ^{13}C NMR (100 MHz) 163.41, 160.95 ($J_{\text{C-F}} = 247.1$ Hz), 139.72, 137.17, 131.68, 131.60 ($J_{\text{C-F}} = 7.9$ Hz), 131.08, 131.05 ($J_{\text{C-F}} = 3.4$ Hz), 128.49, 128.09, 127.93, 127.56, 123.90, 115.70, 115.49 ($J_{\text{C-F}} = 21.4$ Hz); MS (m/e , relative intensity) 340 (M^+ , 100) .

1,8-Bis(4-phenoxybenzoyl)naphthalene.

In a dry 50 mL flask equipped with a stir bar, a Dean-Stark trap fitted with a condenser and a nitrogen inlet, were placed the 1,8-bis(4-fluorobenzoyl)naphthalene (5.000 g, 13.4 mmol) and phenol (2.525 g, 26.8 mmol). TMSO_2 (20 mL) and toluene (7 mL) were added to the flask. Potassium carbonate was then added to the suspension. The mixture was heated up to 140 °C and stirred for 2 hours to distill off the azeotrope formed by water with toluene. The temperature was then increased to 180 °C and the mixture was allowed to react overnight. The reaction was then stopped and the solution was precipitated into a beaker containing methanol (200 mL). The white solids were filtered and then recrystallized twice from toluene-methanol (1:1 v/v) to afford the desired product as white crystalline solids: 5.579 g (80%); mp 181-182 °C; IR (KBr, cm^{-1}) 1649 (C=O), 1244 (C-O-C); ^1H NMR (200 MHz) 8.03 (d d, 2 H, $J_{\text{H-H}} = 7.55$ Hz, $^4J_{\text{H-H}} = 1.93$ Hz), 7.78 (d d, 4 H, $J_{\text{H-H}} = 8.98$ Hz, $^4J_{\text{H-H}} = 2.08$ Hz), 7.55 (m, 4 H), 7.38 (d d, 4 H, $J_{\text{H-H}} =$

8.46 Hz, $J_{\text{H-H}} = 7.75$ Hz), 7.17 (t t, 2 H, $J_{\text{H-H}} = 7.35$ Hz, $^4J_{\text{H-H}} = 1.22$ Hz), 7.07 (d d, 4 H, $J_{\text{H-H}} = 8.60$ Hz, $^4J_{\text{H-H}} = 1.20$ Hz), 6.90 (d d, 4 H, $J_{\text{H-H}} = 8.93$ Hz, $^4J_{\text{H-H}} = 2.11$ Hz); ^{13}C NMR (50 MHz) 196.15, 161.77, 155.18, 136.86, 134.76, 132.57, 131.92, 131.65, 129.88, 129.51, 128.67, 124.74, 124.48, 120.26, 116.57; MS (m/e , relative intensity) 323 ($\text{M}^+ - \cdot\text{COPhOPh}$).

POLYMER SYNTHESIS

Polymerizations were typically carried out in a dry 50 mL, three-necked flask equipped with a stir bar, a Dean-Stark trap fitted with a condenser and a nitrogen inlet, according to methods A and B.

Method A (a typical procedure): In the three-necked flask was placed 1,8-bis(4-fluorobenzoyl)naphthalene (1.117 g, 3.00 mmol) and BPA (0.685 g, 3.00 mmol). Chlorobenzene (2 mL) was used to wash any remaining solids stuck to the opening of the flask. TMSO_2 (4 mL) was added to the content of the flask. Potassium carbonate (0.539 g, 4.90 mmol) was added to the suspension. The temperature was then increased to 230 °C. The azeotrope of chlorobenzene and water was distilled off at 140-150 °C. After one hour, TMSO_2 (4 mL) was added and the reaction continued for 3 hours. The resulting solution was then cooled to 150 °C, diluted with TCE (15 mL) and precipitated into a beaker containing methanol (100 mL) and a few drops of HCl. The polymer was purified by dissolving in chloroform, filtering through a pad of Celite and then precipitating into methanol yielding a powdery polymer after drying in a vacuum oven at 60 °C: 1.606 g (80%).

Method B (a typical procedure): To the dried flask containing 1,8-bis(4-fluorobenzoyl)naphthalene (1.117 g, 3.00 mmol), BPA (0.685 g, 3.00 mmol), deoxygenated toluene (6 mL) and TMSO_2 (4 mL) was added finely ground potassium carbonate (1.036 g, 7.50 mmol). The mixture was stirred at 140-150 °C for 2 hours under a strong flow of nitrogen to azeotrope off the water formed with toluene. The temperature

was then increased to 180 °C. After one hour of reaction and an apparent increase in the viscosity, TMSO₂ (4 mL) was added. The reaction was monitored by testing samples by GPC. After another hour, the reaction was complete, showing no increase in the molecular weight. The reaction mixture was cooled down to 150 °C, diluted with TCE (15 mL) and precipitated into methanol (200 mL) containing a few drops of HCl. The resulting fibrous polymer was dissolved in chloroform (70 mL), filtered through a thin bed of Celite to remove the inorganic salts, and reverse precipitated to remove low molecular weight fractions, yielding white fibrous polymer **III-2a**: 1.634 g.

III-2a: 96%; IR (film, cm⁻¹) 1661 (C=O), 1243 (C-O-C); ¹H NMR (200 MHz) 8.00 (d, 2 H, J_{H-H} = 7.96 Hz), 7.75 (d, 4 H, J_{H-H} = 8.75 Hz), 7.52 (m, 4 H), 7.22 (d, 4 H, J_{H-H} = 8.75 Hz), 6.95 (d, 4 H, J_{H-H} = 8.61 Hz), 6.87 (d, 4 H, J_{H-H} = 8.91 Hz), 1.65 (s, 6 H); ¹³C NMR (50 MHz) 196.29, 161.99, 153.20, 146.84, 137.05, 134.90, 132.75, 132.01, 131.82, 129.68, 128.84, 128.36, 124.93, 119.88, 116.72, 42.40, 31.07.

III-2b: 90%; IR (film, cm⁻¹) 1655 (C=O), 1247 (C-O-C); ¹H NMR (400 MHz) 8.03 (d, 2 H, J_{H-H} = 8.00 Hz, ⁴J_{H-H} = 1.48 Hz), 7.84 (d, 4 H, J_{H-H} = 8.70 Hz), 7.56 (d, 2 H, J_{H-H} = 7.06 Hz, ⁴J_{H-H} = 1.48 Hz), 7.51 (t, 2 H, J_{H-H} = 7.82 Hz), 7.40 (d, 4 H, J_{H-H} = 8.64 Hz), 7.05 (d, 4 H, J_{H-H} = 9.09 Hz), 6.99 (d, 4 H, J_{H-H} = 8.82 Hz); ¹³C NMR (100 MHz) 196.31, 160.55, 156.49, 136.92, 134.98, 133.13, 132.82, 131.97, 129.73, 128.87, 128.79, 124.95, 119.13, 117.90, 63.42.

III-2c: 85%; IR (film, cm⁻¹) 1654 (C=O), 1229 (C-O-C); ¹H NMR (400 MHz) 7.98 (d, 2 H, J_{H-H} = 7.94 Hz), 7.81 (d, 4 H, J_{H-H} = 8.70 Hz), 7.51 (m, 4 H), 7.08 (s, 4 H), 6.92 (d, 4 H, J_{H-H} = 8.69 Hz); ¹³C NMR (100 MHz) 196.30, 161.89, 151.93, 136.99, 134.97, 132.79, 132.33, 131.82, 129.63, 128.70, 124.90, 121.86, 116.68.

III-2d: 92%; IR (film, cm^{-1}) 1654 (C=O), 1243 (C-O-C); ^1H NMR (200 MHz) 7.97 (d, 2 H, $J_{\text{H-H}} = 7.82$ Hz), 7.71 (d, 6 H, $J_{\text{H-H}} = 8.64$ Hz), 7.49- 7.15 (m, 14 H), 6.87 (d, 4 H, $J_{\text{H-H}} = 8.79$ Hz), 6.82 (d, 4 H, $J_{\text{H-H}} = 8.83$ Hz); ^{13}C NMR (50 MHz) 196.33, 161.74, 154.36, 151.11, 142.10, 140.14, 137.12, 134.99, 132.85, 132.27, 131.92, 129.80, 128.93, 128.05, 127.89, 125.14, 126.21, 125.03, 120.48, 120.03, 117.06, 64.65.

III-2e: 89%; IR (film, cm^{-1}) 1655 (C=O), 1236 (C-O-C); ^1H NMR (200 MHz) 8.00 (d, 2 H, $J_{\text{H-H}} = 8.06$ Hz), 7.80 (d, 4 H, $J_{\text{H-H}} = 8.69$ Hz), 7.52 (m, 8 H), 7.11 (d, 4 H, $J_{\text{H-H}} = 8.61$ Hz), 6.94 (d, 4 H, $J_{\text{H-H}} = 8.89$ Hz); ^{13}C NMR (50 MHz) 196.31, 161.69, 154.81, 136.89, 136.64, 134.87, 132.74, 132.22, 131.83, 129.68, 128.74, 128.47, 124.88, 120.61, 116.86.

III-2f: 90%; IR (film, cm^{-1}) 1655 (C=O), 1227 (C-O-C); ^1H NMR (200 MHz) 8.01 (d d, 2 H, $J_{\text{H-H}} = 8.16$ Hz, $^4J_{\text{H-H}} = 2.01$ Hz), 7.84 (d, 4 H, $J_{\text{H-H}} = 8.2$ Hz), 7.52 (m, 4 H), 7.17 (s, 1 H), 6.95 (m, 6 H), 1.36 (s, 9 H); ^{13}C NMR (50 MHz) 196.67, 162.47, 162.19, 151.43, 151.32, 144.19, 137.29, 137.25, 135.26, 133.06, 132.54, 132.42, 132.37, 132.29, 132.09, 130.07, 129.97, 129.06, 125.14, 122.94, 120.31, 119.27, 119.23, 117.33, 116.60, 35.28, 30.39.

END CAPPING EXPERIMENT

POLYMER III-3. To a dry 50 mL, three-necked flask equipped with a stir bar, a Dean-Stark trap with a condenser and a nitrogen provider containing 1,8-bis(4-fluorobenzoyl)naphthalene (1.729 g, 4.646 mmol), bisphenol III-1b (1.546 g, 4.600 mmol), 3,5-di-tert-butylphenol (0.019 g, 0.092 mmol), TMSO_2 (12 mL) and deoxygenated toluene (15 mL) was added finely ground potassium carbonate (1.383 g, 10.0 mmol). The mixture was heated up to 140-150 $^{\circ}\text{C}$ under a strong flow of nitrogen to

remove the azeotrope. The temperature was then increased to 180 °C and held for 2 hours until a viscous solution was formed and GPC of samples taken from the reaction mixture showed no increase in the molecular weight. The reaction mixture was then allowed to cool down to 150 °C, diluted with TCE (15 mL) and precipitated into methanol (200 mL) containing a few drops of HCl. The resulting polymer was dissolved in chloroform (150 mL), filtered through a thin bed of Celite and reverse precipitated, yielding white fibrous polymer 5: 2.944 g (95%); IR (film, cm^{-1}) 1661 (C=O), 1244 (C-O-C); ^1H NMR (400 MHz) 8.02 (d, 2 H, $J_{\text{H-H}} = 8.00$ Hz), 7.84 (d, 4 H, $J_{\text{H-H}} = 8.71$ Hz), 7.53 (m, 4 H), 7.40 (d, 4 H, $J_{\text{H-H}} = 8.60$ Hz), 7.05 (d, 4 H, $J_{\text{H-H}} = 8.95$ Hz), 6.99 (d, 4 H, $J_{\text{H-H}} = 8.74$ Hz), 1.30 (s); ^{13}C NMR (100 MHz) 196.07, 160.31, 156.24, 136.67, 134.73, 132.88, 132.88, 132.57, 131.71, 129.49, 128.62, 128.54, 125.35, 124.70, 122.50, 118.89, 117.66, 63.66, 31.15. The calculation based on the ratio of two peaks at 1.30 and 8.02 ppm in the ^1H NMR spectrum gave a number of units (n) in the polymer of 106 or $M_n = 70,800$. GPC gave $M_n = 52,700$. Inherent viscosity was 0.51 dL/g in chloroform at 25 °C.

Purification of polymer by reverse precipitation

In a large beaker a polymer (1.0 g) was dissolved in chloroform (50 mL) with stirring. To the chloroform solution, methanol (about 50 mL) was added dropwise through a dropping funnel while the solution was stirred rapidly. To the point when the polymer precipitated out as a gummy residue at either the bottom of the beaker or around the stirring bar, the addition was stopped. After removal of the solvent, the polymer was re-dissolved in chloroform (10-20 mL) and precipitated into methanol. The resulting fibrous polymer was filtered and dried under reduced pressure at 60 °C.

POLYMER TRANSFORMATION

Conditions A (cross linking process): A typical procedure was performed as follows: In a 250 mL dried round-bottomed flask fitted with a reflux condenser and a nitrogen provider, was dissolved polymer III-2a (0.500 g, 0.89 mmol) in TCE (50 mL). Lawesson's reagent (0.719 g, 1.78 mmol) was added and the temperature was raised to 110 °C. At early stage of the reaction, the solution turned from light yellow to dark purple as Lawesson's reagent was dissolving, and finally changed to light orange. FTIR spectra were taken to monitor the polymer transformation. After 2 hours at 110 °C, IR showed the disappearance of the ketone peak, the reaction was stopped. The mixture was then concentrated to a volume of about 20 mL by vacuum distillation and precipitated into methanol (100 mL) with stirring. The resulting powder was only very slightly soluble or formed a gel like product in chloroform, TCE, NMP. The polymer was then washed in a Soxhlet with methanol overnight to remove any remaining by-products, and dried under reduced pressure at 60 °C for one day, yielding an orange powder IV-1a: 0.380 g.

Polymer IV-1a, b, d were tested for the presence of sulphur by Lassaigne's test (sodium fusion) and gave a positive result, proving the formation of a cross-link with sulfur.

IV-1a: (81%); IR (KBr, cm^{-1}) 1594, 1497 (C=C), 1236 (C-O-C). IV-1b: (82%); IR (KBr, cm^{-1}) 1598, 1499 (C=C), 1247 (C-O-C). IV-1c: (85%); IR (KBr, cm^{-1}) 1594, 1490 (C=C), 1222 (C-O-C). IV-1d: (79%); IR (KBr, cm^{-1}) 1594, 1496 (C=C), 1237 (C-O-C). IV-1e: (89%); IR (KBr, cm^{-1}) 1594, 1488 (C=C), 1231 (C-O-C). IV-1f: (80%); IR (KBr, cm^{-1}) 1600, 1479 (C=C), 1219 (C-O-C).

Conditions B (no cross linking): A typical procedure was performed following the same procedure as conditions A. The reaction was run in dilute conditions using twice as much solvent and reducing the reaction temperature to 80-90 °C. Longer reaction

conditions were required as followed by IR. After two days of reaction, the reaction was found complete. Similar work-up was effected.

IV-2a: (89 %); IR (KBR, cm^{-1}) 1594, 1499 (C=C), 1238 (C-O-C). **IV-2b:** (88 %); IR (KBR, cm^{-1}) 1597, 1502 (C=C), 1248 (C-O-C). **IV-2d:** (92 %); IR (KBR, cm^{-1}) 1595, 1497 (C=C), 1237 (C-O-C). **IV-2e:** (89 %); IR (KBR, cm^{-1}) 1594, 1489 (C=C), 1234 (C-O-C).

Lassaigne's test

A cube of freshly cut sodium (~0.04 g) was placed in a Pyrex test tube. The test tube was heated steadily until dark-grey sodium vapor rose 2 cm in the test tube. The sample of polymer VI(c) (0.05 g) was then dropped directly on the molten sodium and the test tube was heated to redness for about 2 min. After cooling down, methanol (1 mL) was added to decompose any unreacted sodium, and water (3 mL) was added. The mixture was transferred into a small beaker and methanol was gently evaporated. The residue was crushed with a glass rod to assist in the extraction of the inorganic salts from the fusion residue. The mixture was filtered and the clear filtrate was then acidified with dilute acetic acid. A few drops of lead acetate solution were added, showing no precipitation of black solids of lead sulfide, meaning a negative result for the presence of sulphur.

END

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