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**SYNTHESIS AND CHARACTERIZATION OF POLYIMIDES WITH
NOVEL STRUCTURES**

by

YU QI, B. Eng.

A thesis submitted to
the Faculty of Graduate Studies and Research
in partial fulfilment of the requirements for the degree of
Doctor of Philosophy

The Department of Chemistry
Carleton University

Ottawa, Ontario, Canada

January 10th 1997

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Date Jan 7, 1987

To My Parents

ABSTRACT

The design and synthesis of new monomers is one of the common approaches to the development of high-performance polymers with desirable properties and functions. The design of a new monomer, diphenylprehnitic dianhydride containing a unique bent dianhydride unit, is rationalized based on the structure-property relationship of the resulting polyimides. The synthesis and characterization of a series of novel polyimides derived from diphenylprehnitic dianhydride and a number of aromatic diamines are described. Polyimides with high molecular weights were synthesized by one-step solution polymerization in *m*-cresol, and were readily soluble in many common organic solvents, such as N,N-dimethylacetamide, N-methyl-2-pyrrolidinone, dimethylsulfoxide, and N,N-dimethylformamide, due to the bent diimide unit in the polymer backbone. These polyimides displayed high glass transition temperatures, ranging from 362 to 443 °C. Degradation temperatures for 5% weight loss of the polyimides in all cases occurred above 483 °C in nitrogen and 449 °C in air. Some of the polyimides also showed good mechanical properties, Young's moduli of thin films ranged from 2.07 to 3.94 GPa. Alternating insertion of the bent diimide unit into the rigid-rod backbone can effectively reduce the crystallinity and improve the solubility of very rigid polyimides, as illustrated by a series of copolymers.

This thesis also describes the synthesis of the first AB-type aminoanhydride monomer containing a tetrahydro[5]helicene core. This aminoanhydride was polymerized to the corresponding polyimide in high molecular weight by solution polycondensation. This finding opens a new avenue to the synthesis of other aromatic aminoanhydride monomers. Although the [5]helicene-based polyimide could not be made in high molecular weight directly from the corresponding [5]helicene aminoanhydride by one-step solution polymerization, it was obtained by chemical transformation of the tetrahydro[5]helicene polyimide in both solution and solid state.

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SYMBOLS AND ABBREVIATIONS

BPDA	3,3',4,4'-Biphenyletricarboxylic dianhydride
6FDA	4,4'-(Hexafluoroisopropylidene)diphthalic anhydride
COSY	Correlated spectroscopy
δ	Chemical shift (ppm)
DMAc	N,N-dimethylacetamide
DMSO	Dimethyl sulfoxide
DSC	Differential scanning calorimetry
E'	Young's modulus
GPC	Gel permeation chromatography
HETCOR	Heteronuclear shift correlation
η_{int}	Intrinsic viscosity
HRMS	High resolution mass spectrometry
IR	Infrared
J	Coupling constant (Hz)
MDA	4,4'-Methylenedianiline
Mn	Number-average molecular weight
mp	Melting point
MS	Mass spectrometry
Mw	Weight-average molecular weight
n	Number of units
N ₂	Nitrogen
NMP	1-Methyl-2-pyrrolidinone
NMR	Nuclear magnetic resonance
ODA	4,4'-Oxydianiline
ODPA	Oxydiphthalic anhydride
PAA	Poly(amic acid)
PMDA	Pyromellitic dianhydride
Tan δ	Loss tangent
TCE	1,1,2,2-Tetrachloroethane
Td	Decomposition temperature
Tg	Glass transition temperature
TG	Thermogravimetry

THF	Tetrahydrofuran
TLC	Thin layer chromatography
T _m	Melting temperature
TMA	Thermomechanical analysis
UV	Ultraviolet

CHAPTER I. INTRODUCTION

Aromatic polyimides represent one of the most important classes of high-performance polymers and are characterized as containing a cyclic imide functionality with the general structure shown in Figure I.1. They are usually prepared by a polycondensation reaction of an aromatic dianhydride and an aromatic or aliphatic diamine. Due to the strong bonds within the imide group and a rigid aromatic structure, polyimides have been used for high-temperature applications requiring a high glass transition temperature, high thermal, and thermo-oxidative stability.

Figure I.1. The generic structure of aromatic polyimides.

As such aromatic polyimides have found applications in many fields, such as aerospace, automotive, and microelectronics. They have been used as adhesives, fibers, films, mouldings, composite matrices, coatings and membranes. For example, the most widely used polyimide, commercially known as Kapton® film (Figure I.2), is produced from pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA). Kapton® exhibits many attractive features such as very high tensile strength (172.4 MPa), high tensile modulus (2.1 GPa), and outstanding thermal stability. After heating for 500 h at 300 °C in air, it only loses 4.4 % by weight. It also has a low dielectric constant (3.5 at KHz at 25 °C) and excellent solvent resistance.¹

Scheme I.1. Synthesis of polyimides from a dianhydride and a diamine.

The mechanism of polyimide formation is illustrated using a monofunctional species in Scheme I.2. Nucleophilic attack of the nitrogen of an amine to the carbonyl group of a dianhydride gives an intermediate amic acid which is then converted to the corresponding imide at elevated temperatures or upon treatment with a chemical dehydrating agent such as acetic anhydride.

Scheme I.2. The mechanism of polyimide formation.

For intractable aromatic polyimides, such as most polypyromellitimides derived from PMDA, preparation of a high molecular weight poly(amic acid) is necessary in order to obtain a polyimide with high molecular weight, because direct polyimidization is not possible due to rapid loss of the molecular mobility and solubility at relatively low molecular weight. The formation of the poly(amic acid) is usually carried out in a polar aprotic solvent, such as *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), or *N*-methylpyrrolidinone (NMP) at temperatures from 15 to 75 °C.⁴ The poly(amic acid) is then thermally imidized to produce the final polyimide. A disadvantage in this route is that the poly(amic acid) is hydrolytically unstable. On prolonged storage, a dramatic decrease in molecular weight is observed, which causes loss of physical properties in the final polymer.

In contrast, polyimides with good tractability, for example some flexible poly(ether imide)s, have been obtained by melt polymerization⁵ or by a one-step solution process in a high-boiling organic solvent, such as *m*-cresol, at 180–220 °C.^{6,7} The formation of a high molecular weight poly(amic acid) is not necessary as long as the reaction system maintains homogeneity in the melt or in solution. The water generated from imidization is usually distilled off from the reaction mixture. With an increase in the need for improving processability of polyimides, the one-step solution synthesis becomes more and more important because it can produce soluble polyimides in bulk.

I.1.1b. Polyimides Synthesized by Other Methods

Polyimides can also be synthesized using other methods involving imide bond formation and are outlined in Table I.1.

Table I.1. Other synthetic methods for polyimides.

Methods	Reaction Scheme
A. ^{8, 9, 10}	$ \begin{array}{c} \text{HO}-\text{C}(=\text{O})-\text{Ar}-\text{C}(=\text{O})-\text{X} \\ \text{X}=\text{OH, OR} \end{array} + \text{H}_2\text{N}-\text{Ar}'-\text{NH}_2 \rightarrow \left[\text{HN}-\text{C}(=\text{O})-\text{Ar}-\text{C}(=\text{O})-\text{NH}-\text{Ar}' \right]_n \xrightarrow{\Delta} \left[\text{N}-\text{C}(=\text{O})-\text{Ar}-\text{C}(=\text{O})-\text{N}-\text{Ar}' \right]_n $ PAA
B. ^{11, 12, 13}	$ \text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_2(\text{COOH})_2 \xrightarrow{(\text{ArO})_3\text{P}} [\text{PAA}] \xrightarrow{\Delta} \left[\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_2(\text{CO})_2-\text{N} \right]_n $
C. ^{14, 15, 16}	$ \text{O}=\text{C}-\text{Ar}-\text{C}(=\text{O})-\text{O} + \text{OCN}-\text{Ar}'-\text{NCO} \xrightarrow{-\text{CO}_2} \left[\text{N}-\text{C}(=\text{O})-\text{Ar}-\text{C}(=\text{O})-\text{N}-\text{Ar}' \right]_n $
D. ^{17, 18}	$ \text{X}-\text{C}_6\text{H}_3(\text{N}=\text{Ar}'-\text{N})_2-\text{X} + ^-\text{O}-\text{Ar}'-\text{O}^- \xrightarrow{\text{X} = \text{halogen, } -\text{NO}_2} \left[\text{C}_6\text{H}_3(\text{N}=\text{Ar}'-\text{N})_2-\text{O}-\text{Ar}'-\text{O} \right]_n + \text{X}^- $
E. ^{19, 20, 21}	$ \text{HN}-\text{C}(=\text{O})-\text{Ar}-\text{C}(=\text{O})-\text{NH} + \text{H}_2\text{N}-\text{R}-\text{NH}_2 \rightarrow \left[\text{RHN}-\text{C}(=\text{O})-\text{Ar}-\text{C}(=\text{O})-\text{NHR} \right]_n \rightarrow \left[\text{N}-\text{C}(=\text{O})-\text{Ar}-\text{C}(=\text{O})-\text{N}-\text{R} \right]_n + \text{NH}_3 $
F. ²²	$ \text{I}-\text{C}_6\text{H}_2(\text{COOBu}^t)_2 + \text{H}_2\text{N}-\text{Ar}'-\text{NH}_2 \xrightarrow[\text{DBU/CO/DMAc}]{\text{PdCl}_2\text{L}_2/\text{PPh}_3} \left[\text{N}-\text{C}_6\text{H}_2(\text{CO})_2-\text{N}-\text{Ar}' \right]_n $
G. ²³	$ \text{NC}-\text{C}_6\text{H}_2(\text{CN})_2-\text{C}_6\text{H}_2(\text{CN})_2-\text{NC} + \text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-\text{NH}_2 \xrightarrow{\text{NMP}} \left\{ \text{Partially imidized poly(amic acid)-like intermediate} \right\} \xrightarrow{\Delta} \left[\text{N}-\text{C}_6\text{H}_2(\text{CO})_2-\text{N}-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4 \right]_n $ Kapton

These synthetic approaches reported in the literature are for some specific cases. Method B is the so-called phosphorylation method, which offers access to a self-condensation polyimide from an aminoaryldicarboxylic acid and also to a polyimide from an aromatic diamine and a tetracarboxylic acid. In general, the aminoanhydride monomers are very difficult to obtain in high purity because of the high reactivity between the anhydride and amino groups.

In method C, a diisocyanate reacts with a dianhydride only at high temperatures (180 °C), but in the presence of a catalytic amount of water or alcohol the reaction goes faster at lower temperatures.

A nucleophilic displacement reaction carried out with a bis(haloimide) or bis(nitroimide) and a bisphenol (Method D) is a practical approach to the synthesis of poly(ether imide)s, involving no imide formation during the course of polymerization. This process is used to produce Ultem® engineering thermoplastics, a G. E. product.

Transimidization (Method E) works similar to a condensation reaction. The intermediate is a poly(amic amide) instead of a poly(amic acid). During the polycondensation reaction, ammonia is released, instead of water.

Methods F and G have recently been developed as a low temperature process producing polyimides in one step. Methods F is based on a palladium-catalyzed carbonylation, allowing for the formation of a high molecular weight polyimide at 120 °C. Methods G produces a prepolymer at room temperature containing 75% of the imide component which is subsequently cured at elevated temperatures.

I.1.2. Synthesis of Addition Polyimides

Addition polyimides are crosslinked polymers, derived from monomeric or oligomeric imides, which are functionalized with reactive end-groups capable of undergoing polymerization by thermal or catalytic means to form a highly crosslinked

polyimide. These materials cannot be remelted under any pressure, and are therefore referred to as thermosetting polyimides (or thermoset resins).

Chain propagation for this type of polyimide is not based on the formation of the imide functionalities. Rather, it depends on reactive end-groups which function as chain extenders which undergo addition polymerization. Addition polyimides are classified according to their reactive end-groups, maleimide, acetylene, benzocyclobutene, and nadimide. An addition polyimide is synthesized via a classical route, reacting a dianhydride or its derivatives with an aromatic diamine in the presence of a monofunctional end-group. The resulting preformed imide monomer or oligomer is further cured producing a crosslinked polymer, as illustrated in Scheme I.3.

Scheme I.3. Synthesis of the addition polyimides.

I.2. Structural Modification of Polyimides

Aromatic polyimides have found various applications as mentioned previously. This is due in part to aromatic polyimides possessing high thermal stability, heat resistance and good mechanical properties. Research has been conducted not only to develop synthetic methods to produce polyimides, but also to change the properties of polyimides. Due to their inertness toward organic solvents and heat resistance, many aromatic polyimides have poor processability. Therefore, structural modification of polyimides with the intent to improve processability, has been one of the main focuses of research in this area.

I.2.1. General Problems Associated with Polyimides

The general fabrication process for a polymeric material requires that the polymers be either molten below their decomposition temperature for a molding extrusion process, or soluble in an organic solvent for a casting process. However, aromatic polyimides, such as poly(pyromellitimide)s, are generally insoluble and infusible. As a result, they are very difficult to be fabricated in their imide form.

Although the structure-solubility relationship for polyimides is not fully understood, extensive studies have looked at the effects that chemical structure has on the properties of polyimides. They have revealed that certain structural features, such as the rigidity of the polyimide backbone, strong interaction between polymer chains and crystallinity, are responsible for high softening and melting temperatures, and insolubility. The interactions between polyimide chains are induced by electronic polarization and crystalline interaction.²⁴ Figure I.3 shows two kinds of interactions. Either one of the interactions can result in tighter packing between the polymer chains and will serve to increase melt temperature and the insolubility of the polymer. For example, a rigid-rod polyimide, polypyromellitimide (derived from *p*-phenylenediamine and PMDA, Figure I.4), has an extremely high calculated glass transition temperature (T_g , 702 °C) and a

calculated melting point (T_m , 1027 °C).²⁵ These values could not be confirmed experimentally since they are above the decomposition temperature of the polyimide.

Figure I.3. The chain-chain interaction of polyimides.

Figure I.4. Calculated T_g and T_m of polypyromellitimide.

In order to fabricate a rigid-rod aromatic polyimide, it is necessary to process it in the form of its soluble poly(amic acid) precursor, which is then subsequently thermally imidized. However, this practice limits the application of polyimides to the form of thin films and coatings. The fabrication of large, thick parts using this method is complicated by the evolution of the water during imidization. Also, the poly(amic acid) solutions are

unstable to moisture during storage and must be handled with care. Therefore, it is desirable to have melt processable or soluble polyimides that maintain their high thermal stability.

One of the major research tasks, in the area of polyimides, is structural modification of the dianhydride and/or diamine monomers, aimed at the development of aromatic polyimides that can be melt and/or solution processed. However, thermal properties, such as high T_g and thermal stability, are usually inversely related to solubility and ease of processing. That is, if the solubility increases, the T_g and thermal stability decrease. For example, the polyimide containing a C=O bridge and an aliphatic linkage illustrated in Figure I.5 is soluble in organic solvents like NMP, DMAc, and DMF, but its T_g is only about 150 °C and T_m is about 240 °C,²⁶ which are much lower than that of the rigid PMDA-*p*-phenylenediamine polyimide (Figure I.4). Because the polyimide contains an aliphatic chain, its decomposition temperature is low (ca. 400 °C), where normal aromatic polyimides decompose at about 500 °C in a inert atmosphere.

Figure I.5. Polyimide containing aliphatic linkages.

Therefore, it is desirable and also challenging to increase solubility while maintaining high temperature properties of aromatic polyimides. The main approaches used for structural modifications include:

- (1) introduction of a flexible, thermally stable unit into the polymer chain;
- (2) incorporation of large polar or non-polar substituent into the polymer backbone;
- (3) disruption of symmetry and recurring regularity in the polymer backbone through copolymerization of two dianhydrides or two diamines.

I.2.2. Polyimides Containing Flexible Linkages

A common approach to increase the flexibility of the polymer chain is to introduce a flexible unit into either a diamine or a dianhydride monomer. Some examples of aromatic diamines and dianhydrides with flexible linkages are shown in Figure I.6.

Figure I.6. Examples of diamine and dianhydride monomers with flexible linkages.

Polyimides with aliphatic linkages, such as those derived from MDA (Figure I.6), usually have lower thermal stability. In order to maintain good thermal stability, it is common to use flexible units containing thermally stable groups, such as “O”, “C=O”, “O=S=O”, “S”, and “C(CF₃)₂” (6F). The 6F group is especially interesting, since

incorporation of the 6F unit into the polymer chain usually increases the solubility, thermal stability, flame resistance, and oxidation resistance, while decreasing the crystallinity.²⁷ High thermal stability of the 6F-containing polyimides is attributed to the strong C-F bond. However, the 6F-containing monomers are usually expensive, which consequently limits the scope of applications of 6F-containing polyimides. Dianhydrides with a phosphorous linkage (DA-a in Figure I.6) have also been used to produce soluble polyimides which exhibited high thermal stability.²⁸

Some commercial polyimides containing thermally stable, flexible units are depicted in Figure I.7.

Figure I.7. Examples of some commercial polyimides.

Although the rigidity and the interchain interaction of polyimides can effectively be reduced by incorporating flexible linkages into the polymer backbone, the high-temperature performance associated with the rigid parent polymers is compromised with the increased flexibility of the polymer chains. Comparing with the polyimide derived from PMDA and *p*-phenylenediamine, these commercially available polyimides have much lower T_g 's as shown above.

The solubility of polyimides can be also dramatically affected by the incorporation of a kink in the polyimide backbone through *ortho* or *meta* catenation. As the backbone flexibility increases, the solubility of polyimide increases. This is most apparent with *ortho* catenation and to a lesser extent with *meta* catenation. *Para* catenation results in the least soluble polyimides because of its linearity. For example, the polyimides derived from *m*-phenylenediamine are generally more soluble than those derived from *p*-phenylenediamine. Furthermore, among the polyimides derived from 3,3'-, 3,4'-, and 4,4'-oxydiphthalic anhydrides (ODPA) (Figure I.8), the less linear polyimide (from 3,4'-ODPA) is more soluble than the one derived from 4,4'-ODPA. The dianhydride with *ortho* catenation (3,3'-ODPA), the least linear one, produces the most soluble polyimides.²⁹ Moreover, 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) and its isomer, 2,2',3,3'-biphenyltetracarboxylic dianhydride are two kinked monomers (Figure I.9).³⁰ Their structures contain a single bond between two phthalic anhydrides which can be freely rotated, and therefore these two dianhydrides have a non-planar structure which brings improved solubility to the resulting polyimides. Comparing the polyimide derived from these two dianhydrides, the former is more linear than the later one, and consequently has poorer solubility. Although the *ortho* or *meta* catenation and an ether linkage could impart a higher degree of solubility to the polyimides, again, the Tg's are lower when the polymers become more flexible.

Figure I.8. Isomeric ODPA monomers.

Figure I.9. Kinked and rigid biphenyl dianhydrides (BPDA).

I.2.3. Polyimides Containing Large Non-polar and Polar Pendant Groups

Incorporating bulky pendant groups along the polyimide chain can inhibit chain packing and therefore allow less interaction to occur between the polymer chains. As a result, the solubility of the polymers increases while the high temperature properties remain because the overall polyimide chain is still rigid. Both diamine and dianhydride monomers containing various non-polar and polar pendant groups have been synthesized and polymerized to produce soluble yet rigid polyimides.

The improvement in solubility depends on the nature of the non-polar pendant groups, as seen in the following examples. The polyimide derived from PMDA and *m*-phenylenediamine is an insoluble material. However, once the isopropyl group is introduced in *m*-phenylenediamine, the resulting polyimide was soluble in DMF. With the larger anthracene as a pendant group, the polyimide became even more soluble (Table I.2).³¹

Table I.2. Effect of pendant groups on the solubility of the polyimides.

Dianhydride	PMDA	PMDA	PMDA
Diamine			
Solvent for the polyimide	Insoluble	DMF	DMF, DMAc, DMSO, NMP

A series of twisted diamines, 2,2'-disubstituted-4,4'-diaminobiphenyls (Figure I.10), such as 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl,³² 2,2'-dimethyl-4,4'-diaminobiphenyl,³³ 2,2'-diphenyl-4,4'-diaminobiphenyl and 2,2'-bis[4-(trifluoromethyl)phenyl]-4,4'-diaminobiphenyl,³⁴ have been recently synthesized to produce soluble, high-strength polyimides. The substituted group at the 2, 2'-positions of biphenyl sterically forces the two aromatic rings into a non-planar conformation. Such nonplanarity causes a decrease in the polymer's crystallinity, which leads to enhanced solubility, while the high temperature properties associated with rigid-rod polyimides remain. Among the diamines, 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl, stands out for its ability to impart solubility and maintain the rigidity of the polyimides. However, the solubility of the polyimides resulting from these twisted diamine monomers can only be improved to certain extent. When the very rigid PMDA was polymerized with 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl, the resulting polyimide remained insoluble in common organic solvents.

Figure I.10. 2,2'-Disubstituted-4,4'-diaminobiphenyls.

Several twisted dianhydrides, 2,2-disubstituted-4,4',5,5'-biphenyltetracarboxylic dianhydrides (Figure I. 11), 2,2'-dibromo-4,4',5,5'-biphenyltetracarboxylic dianhydride and 2,2'-bis(trifluoromethyl)-4,4',5,5'-biphenyltetracarboxylic dianhydride,³⁵ have also been developed. The polyimides, obtained from a twisted dianhydride and some of the twisted diamines mentioned above, contain a segmented rigid-rod structure while being soluble in acetone and tetrahydrofuran. These soluble polyimides can be readily solution cast into colourless thin films which found application as the retardation layer for liquid crystal displays.³⁶

Figure I.11. 2,2-Disubstituted-4,4',5,5'-biphenyltetracarboxylic dianhydrides.

Polar pendant groups have also been introduced into the polyimide chain to improve the solubility. Polyimides with polar substituents tend to be more soluble in polar solvents.³⁷ For instance, the modified 4,4'-benzidine with benzoylimino group (Figure I.12) has been synthesized and polymerized with a series of aromatic dianhydrides.³⁸ It was found that the solubility of the polyimides was significantly improved, but the rigid-rod polyimide derived from PMDA was only soluble in conc. H_2SO_4 and methanesulfonic acid.

Figure I.12. 2-(N-benzoylimino)-4,4'-diaminobiphenyl.

A series of polyimides have been prepared from a phenylated dianhydride (Figure I.13) with various diamines by one-step solution polymerization.³⁹ The polyimides derived from the diamines which contain flexible or meta linkages could be dissolved in common organic solvents. However, the polyimide from the rigid diamine, *p*-phenylenediamine, was still insoluble in hot *m*-cresol during polymerization, and therefore only oligomers were obtained.

Figure I.13. A phenylated dianhydride.

Being the smallest and most rigid dianhydride, PMDA has recently been subjected to structural modifications by introduction of pendant groups, aimed at increasing the solubility of poly(pyromellitimide)s without substantially decreasing the rigidity. In PMDA only the 3,6-positions are available for functionalization. Conceivably, substitutions of PMDA at the 3,6-positions would produce a series of monomers for a variety of new polyimides with different properties. PMDA has been modified by introducing phenyl,⁴⁰ trifluoromethyl,⁴¹ trifluoromethoxy,⁴² 3-trifluoromethylphenyl and 4-trifluoromethylphenyl⁴³ groups at the 3,6-positions (Figure I.14). It was found that polyimides based on diphenylpyromellitic dianhydride (PMDA-b) with aromatic diamines

containing flexible ether or methylene linkages, meta-catenation, or cardo linkages were organo-soluble and could be synthesized using one-step solution polymerization. Poly(pyromellitimide)s derived from the 3,6-substituted PMDA with rigid diamines such as *p*-phenylenediamine and 4,4'-diaminobiphenyl remained insoluble in common organic solvents and were only prepared via their poly(amic acid) precursors.

Figure I.14. The structures of PMDA and 3,6-substituted PMDA.

I.2.4. Soluble Copolyimides Derived From Two Dianhydrides or Two Diamines

Copolymerization is an alternative way to modify polymer properties to meet a specific requirement. The disruption of symmetry and recurring regularity through copolymerization of two dianhydrides or two diamines can reduce the chain-chain interaction and crystallinity of rigid polyimides. Consequently, copolymerization is one of the most convenient methods to improve the solubility of polyimides. It is especially desirable to use a copolymerization method for improving the solubility of poly(pyromellitimide)s derived from the stiff diamines (*p*-phenylenediamine or 4,4'-benzidine). In the past, all efforts towards structural modifications on PMDA or on *p*-phenylenediamine and benzidine failed to result in organo-soluble poly(pyromellitimide)s without introducing flexible linkages within the polymer chain. To maintain the rigidity of poly(pyromellitimide)s, it is preferable to use a second dianhydride, in as small a ratio as possible, to make the copolyimides soluble while retaining the inherent high temperature properties of poly(pyromellitimide)s. However, the best results reported so far are

copoly(pyromellitimide)s containing at least 50% of the other flexible dianhydride with, in most cases, diamines containing flexible linkages. For example, copolyimides synthesized from PMDA, BPDA and 9,9'-bis(4-aminophenyl)fluorene were soluble in amide solvents and 1,1,2,2-tetrachloroethane (TCE), when the BPDA content reached above 50 mol%.⁴⁴ A recent report described the synthesis of perfectly alternating copolyimides via amic ester precursors, from PMDA and 6FDA with *m*-phenylenediamine and *p*-phenylenediamine.⁴⁵ The resulting alternating copolyimides were more soluble than the corresponding random ones.

References

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1. Hergenrother, P. M. *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1262.
  2. Bogert, T. M.; Renshaw, R. R. *J. Am. Chem. Soc.* **1908**, *30*, 1140.
  3. (a) Edwards, M. W.; Robinson, I. M. U.S. Pat. 2710853 to E. I. DuPont de Nemours & Co.; 1955. (b) Hirsch, S. S.; Lilyquist, M. R. *J. Appl. Polym. Sci.*, **1967**, *11*, 305. (c) Lee, H.; Stofey, D.; Neville, K. *New Linear Polymers*, McGraw-Hill, New York, 1967.
  4. (a) Bessonov, M. I.; Koton, M. M.; Kudryavtsev, V. V.; Laius, L. A. *Polyimides: Thermally Stable Polymers*, 2nd Ed., Plenum, New York, 1987, pp 1-95. (b) Bower, G. M. and Frost, L. *J. Polym. Sci., Part A.* **1963**, *1*, 3135. (c) Dine-Hart, R. A.; Wright, W. W. *J. Appl. Polym. Sci. II*, **1967**, 609. (d) Jones, J. I.; Ochynski, F. W.; Tackley, F. A. *Chem. Ind.* **1962**, 1686.

-
5. Takekoshi, T.; Kochanowski, J. E. *U.S. Pat.* 3,833,546 to G. E., 1974.
6. (a) Beck, Co., French Pat. 1,373,383, 1964; *Chem. Abstr.* 62:10636. (b) Harris, F. W.; Norris, S. O.; Lanier, L. H.; Reinfardt, B. A.; Case, R. D.; Varaprath, S.; Padaki, S. M.; Torres, M.; Feld, W. A. in *Polyimides: Synthesis, Characterization and Applications*, Vol I, Ed. Mittal, K. L., Plenum, New York, 1984, pp 3-14.
7. Takekoshi, T.; Kochanowski, J. E. *U.S. Pat.* 3,905,942 to G. E., 1975.
8. Edwards, M. W.; Robinson, I. M. *U.S. Pat.* 2867609 to E. I. DuPont de Nemours & Co., 1959
9. (a) Lauver, R. W. *J. Polym. Sci., Part A.* **1979**, *17*, 2529. (b) Jonhston, J. C.; Meador, M. A. B.; Alston, W. B. *J. Polym. Sci., Polym. Chem.* **1987**, *25*, 2175.
10. (a) Kharkov, S. N.; Krasnov, E. P.; Laurova, Z. N.; Baranova, S. A.; Aksenova, U. P.; Chegola, A. S. *J. Polym. Sci. USSR*, **1971**, *13*, 940, *Chem. Abstr.* 75:21065p. (b) Becker, K. H.; Schmidt, H. W. *Polym. Mat. Sci. Eng.*, **1992**, 303.
11. (a) Yamazaki, N.; Higashi, F. *Polym. Lett.*, **1974**, *12*, 185. (b) Yamazaki, N.; Higashi, F. *Polym. Preprints. (Am. Chem. Soc. Div. Polym. Chem.)* **1977**, *17 (1)*, 157. (c) Higashi, F.; Akiyama, N.; Ogata, S. *J. Polym. Sci. Polym. Chem.* **1983**, *21*, 913.
12. Nosova, G. I.; Zhukova, T.I.; Koton, M. M.; Lauis, L. A.; Sazanov, Y. N. *Vysokomol. Soedin. Ser. A.*, **1984**, 226, 998, *Chem. Abstr.* 101:91552z.

-
13. (a) Yamazaki, N.; Higashi, F.; Kawabata, J. *J. Polym. Sci., Part A*. **1974**, *12*, 2149.
(b) Yamazaki, N.; Matsumoto, M.; Higashi, F. *J. Polym. Sci., Part A*. **1975**, *13*, 1373.
(c) Higashi, F.; Ogata, S.; Aoki, Y. *J. Polym. Sci., Part A*. **1982**, *20*, 2081.
14. Wartz, A. *Ann. Chem. Phys.* **1954**, *42*, 54.
15. (a) Meyers, R. A.; *J. Polym. Sci., Part A*. **1969**, *7*, 2757. (b) Farrisey, W. J.; Rose, J. M.; Carleton, P. S. *J. Appl. Polym. Sci.*, **1970**, *14*, 1093. (c) Carleton, P. S.; Farisey, W. S.; Rose, J. S. *J. Appl. Polym. Sci.* **1972**, *16*, 2983. (d) Carleton, P. S.; Farisey, W. S.; Rose, J. S. *Ger. Pat.* 2001914 to Upjohn Co., 1970.
16. Merten, R. *Angew. Chem. Int. Ed. Engl.* **1971**, *10*, 294.
17. (a) Wirth, J. G.; Heath, D. R., *U.S. Pat.* 3,787,364 to Gereal Electric, 1974. (b) Williams, F. J., *U.S. Pat.* 3,847, 869 to General Electric, 1974.
18. (a) Wirth, J. G.; Heath, D. R., *U.S. Pat.* 3,838,097 to Gereal Electric, 1974. (b) Takekoshi, T.; Wirth, J. G.; Heath, D. R.; Kochanowski, J. E.; Manello, J. S.; Webber, M. J. *J. Polym. Sci., Part A*. **1980**, *18*, 3069. (c) White, D. M.; Takekoshi, T; Williams, F. J.; Relles, H. M.; Donahue, P. E.; Klopfer, H. J.; Louks, G. R.; Manello, J. S.; Matthews, R. O.; Schluez, R. W. *J. Polym. Sci., A*. **1981**, *19*, 1635.
19. (a) Spring, F. S.; Woods, J. C. *J. Chem. Soc.*, **1945**, 625. (b) Spring, F. S.; Woods, J. C. *Nature*, **1946**, *158*, 754.
20. Saidenova, S. B.; Zhuvanov, B. A.; Arkhipova, I. A.; Rafikov, S. R. *Polym. Sci. USSR*, **1975**, *17*, 1653, *Chem Abstr.* 83:64634z.

-
21. (a) Imai, Y. *Polym. Lett.*, **1970**, *8*, 555. (b) Imai, Y. *Jap. Pat.* 74, 12357 to Teijin Ltd. 1974, *Chem. Abstr.* 73:19481, 121781.
22. (a) Perry, R. J.; Wilson, B. D.; Turner, S. R.; Blevins, R. W. *Macromolecules*, **1995**, *28*, 3509. (b) Perry, R. J.; Turner, S. R.; Blevins, R. W. *Macromolecules*, **1992**, *25*, 4819. (c) Perry, R. J.; Wilson, B. D. *Macromolecules*, **1994**, *27*, 40. (d) Perry, R. J.; Turner, S. R.; Blevins, R. W. *Macromolecules*, **1994**, *27*, 1509.
23. Kim, J-H.; Moore, J. A. *Macromolecules*, **1993**, *26*, 3510.
24. Wilson, D.; Stenzenberger, H. D.; Hergenrother, P. M. *Polyimides*, Blackie and Son: Glasgow, 1990, pp 58.
25. Yang, H. H. *Aromatic High Strength Fibers*, Wiley, New York, 1989.
26. Harris, F. W.; Beltz, M. W.; Hergenrother, P. M. *SAMPLE J.*, **1987**, *23 (1)*, 6.
27. Cassidy, P. E. J. *Macromol. Sci., Rev. Macromol. Chem. Phys.*, **1994**, *C34*, 1.
28. Fedotova, O. Ya.; Gorokhov, V. I.; Paresishvili, O. I.; Karetnikor, G. S. *Vysokomol. Soedin., A*, **1972**, *14*, 1256, *Chem. Abstr.* 77:89002n.
29. Gerber, M. K.; Pratt, J. R.; St. Clair, T. L. in *Polyimides: Materials, Chemistry and Characterization*, Feger, C.; Khojasteh, M.; McGrath, J., Eds.: Elsevier: Amsterdam, 1989; pp 487.

-
30. Rusanov, A. L.; Batirov, I. *Rus. Chem. Rev.* **1980**, *49*(12), 1204.
31. Harris, F. W.; Lanier, L. H. *Structure-Solubility Relationships in Polymer*, Harris, F. W.; Seymour, R. B. Eds. Academic Press: New York, 1977, pp 183.
32. (a) Harris, F. W.; Hsu, S. L.; Tso, C. C. *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **1990**, *31*(1), 342. (b) Matsuura, T.; Hasuda, Y.; Nishi, S.; Yamada, N. *Macromolecules*, **1991**, *24*, 5001. (c) Matsuura, T.; Yamada, N.; Nishi, S.; Hasuda, Y. *Macromolecules*, **1993**, *26*, 419. (d) Cheng, S. Z. D.; Lee, S.; Barley, J.; Hsu, S.; Harris, F. W. *Macromolecules*, **1991**, *24*, 1883. (e) Cheng, S. Z. D.; Arnold Jr., F. E.; Zhang, A.; Hsu, S. L.-C.; Harris, F. W. *Macromolecules*, **1991**, *24*, 5856.
33. Eashoo, M.; Wu, Z.; Zhang, A.; Shen, D.; Wu, C.; Cheng, S. Z. D.; Harris, F. W. *Macromolecular Chemistry and Physics*. **1994**, *195*, 2207.
34. Chen, J. C. Ph.D. Thesis, The University of Akron, 1996.
35. Lin, S. H.-C. Ph.D. Thesis, The University of Akron, 1994.
36. Harris, F. W.; Cheng, S. Z. D. *U.S. Pat.* 5,344,915; 1994.
37. (a) Imai, Y.; Koga, H. *J. Polym. Sci. A. Polym. Chem.* **1973**, *11*, 2623. (b) Korshak, V. V.; Rusanov, A. L.; Tugushi, D. S.; Gitis, S. S.; Ivanov, A. V.; Botkina, Y. V. *Vysokomol. Soedin., A*, **1972**, *14* (3), 686, *Chem. Abstr.* 77:20078z. (c) Korshak, V. V.; Rusanov, A. L.; Katsarava, R. D.; Niyazi, F. F. *Polym. Sci. USSR*, **1973**, *15*,

-
3000. Vinogradova, S. V.; Slonimskii, G. L.; Vygodskii, Ya. S.; Askadskii, A. A.; Mzhel'skii, A. I.; Churochkina, N. A.; Korshak, V. V. *Polym. Sci. USSR*, **1969**, *11*, 3098, *Chem. Abstr.* 80:109032q.
38. Tan, L.-S.; Simko, S. R. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1995**, *36 (1)*, 441.
39. Harris, F. W.; Feld, W. A.; Lanier, L. H. *J. Polym. Sci., Polym. Let. Ed.*, **1975**, *13*, 283.
40. (a) Harris, F. W.; Hsu, S. L. C. *High Perf. Polym.* **1989**, *1*, 3. (b) Giesa, R.; Keller, U.; Eiselt, P.; Schmidt, H.-W. *J. Polym. Sci., Polym. Chem.* **1993**, *31*, 141.
41. Matsuura, T.; Ishizawa, M.; Hasuda, Y.; Nishi, S. *Macromolecules*, **1992**, *25*, 3540.
42. Auman, B. C. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1994**, *35 (2)*, 749.
43. Tomikawa, M.; Cheng, S. Z. D.; Harris, F. W. . *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1994**, *35 (2)*, 707.
44. Vinogradova, S. V.; Churochkina, N. A.; Vygodskii, Ya. S.; Korshak, V. V. *Vysokomol. Soedin.*, **1973**, *15*, 1713.
45. (a) Rhee, S. B.; Park, J. W.; Moon, B. S.; Chang, J. Y. *Macromolecules*, **1993**, *26*, 404. (b) Park, J. W.; Lee, M.; Lee, M.-H.; Liu, J. W.; Kim, S. D.; Chang, J. Y.; Rhee, S. B. *Macromolecules*, **1994**, *27*, 3459.

CHAPTER II. POLY(ARYL PREHNITIMIDE)S

Structural modifications of aromatic polyimides have been reviewed in Chapter I. Organo-solubility of an aromatic polyimide resulting from structural modifications, not only offers good processability but also allows it to be produced by a one-step solution polycondensation. However, it still remains to be seen if a soluble polyimide would maintain its high-temperature properties. This chapter presents the synthesis of a novel series of polyimide, poly(aryl prehnitimide)s, which are designed to possess high solubility in common organic solvents, high thermal stability and high glass transition temperatures. The design of a new monomer is rationalized based on a structure-property relationship. The synthesis and characterization of the dianhydride monomer, and the resulting polyimides are also discussed in detail.

II.1. Rationale and Objectives

Common strategies for structural modification of aromatic polyimides include insertion of flexible linkages into the polymer backbone and incorporation of pendant groups on the polymer chain, as shown in the following “cartoon” picture (Figure II.1, cases a and b).

Figure II.1. Schematic presentation of structural modifications of polyimides.

Although introduction of flexible units into the polyimide backbone should warrant the formation of a more soluble polyimide, it may also cause a decrease in high-temperature performance (Case a, Figure II.1). Incorporation of large pendant groups along the rigid polyimide chain would be an ideal strategy, in order to increase the solubility of a polyimide while maintaining its high-temperature properties. Poly(diphenyl pyromellitimide) synthesized from diphenylpyromellitic dianhydride (PMDA-b, Figure I.14) and an aromatic diamine is a good example of this approach. However, when rigid diamines (e.g., *p*-phenylenediamine) were used, the resulting polyimides were still insoluble in common organic solvents (Case b, Figure II.1). This implies that the linearity of the planar pyromellitimide structure may dominate overall solubility of rodlike aromatic

poly(pyromellitimide)s. The twisted pendant phenyl groups on PMDA-b can enhance solubility only to a certain extent. Obviously, there is a need for a different structural feature which can deliver further improvements in solubility without decreasing the thermal stability and T_g of the resulting polyimides. It is deemed that the linearity of the rodlike polymer backbone has to be disrupted in order to further improve solubility while the rigidity of the overall polyimide chain has to be maintained for retention high-temperature properties of the polyimides. Therefore, the new feature should contain a rigid bent diimide structure (Case c, Figure II.1). The overall polymer chain is therefore, still rigid while being in a zigzag shape. Then, what is a suitable molecular structure?

Considering only structural modification of a dianhydride monomer, it is recognized that adjusting the position of the two anhydride groups in pyromellitic dianhydride, namely, moving the two anhydride groups close in proximity, is a structural alternation that would result in a polyimide with a rigid zigzag shape.

The general structure of the proposed polyimides and the required dianhydride monomer are illustrated in Figure II.2. The nonlinear diimide unit in the polymer backbone should still be rigid because of the fused heterocyclic imide rings. This bent diimide could help retain the high-temperature performance of aromatic polyimides while increasing the solubility of the corresponding polyimides by reducing the interchain interaction because of its zigzag shape. The two pendant phenyl groups should have a larger twist angle than that in diphenyl-PMDA, because the steric hindrance between two aromatic rings in a *o*-terphenyl unit is larger than that in a “*p*-terphenyl” unit for the latter case. Moreover, the *o*-terphenyl structure should result in improved solubility by preventing the polymer chain from close packing. The pendant aromatic phenyl groups should also increase thermal stability of the polyimides. The required dianhydride monomer, diphenylprehnitic dianhydride, or 5,6-diphenylbenzene-1,2,3,4-tetracarboxylic dianhydride, is a structural isomer of diphenylpyromellitic dianhydride. Aromatic polyimides based on prehnitic dianhydride are still unknown, except for an ill-defined, water-soluble copolymer derived

from PMDA and prehnitic dianhydride with 3,3'-diaminodiphenylether described in a patent.¹ The successful incorporation of diphenylprehnitic dianhydride monomer into a polyimide may also open a route to improvement of the solubility of very rigid polyimides such as the polypyromellitimide derived from *p*-phenylenediamine by copolymerization.

Figure II.2. The proposed bent polyimides and the required dianhydride monomer.

The objectives of the present research are (1) to design and synthesize, from readily available starting materials, novel diphenylprehnitic dianhydride that can impart greater solubility to the resulting polyimide, (2) to synthesize and characterize a series of polyimides derived from the new dianhydride monomer, and (3) to investigate the effect of an alternate bent structure on the properties of some perfectly alternating rigid copolyimides.

II.2. Monomer Synthesis

II.2.1. Retrosynthetic Analysis

The retrosynthetic analysis for diphenylprehnitic dianhydride (**II-1**) is shown in Scheme II.1. The crucial step is construction of the central aromatic ring. Diels-Alder reaction of the cyclone **II-2** and a dienophile such as the diethyl acetylenedicarboxylic diester, provides an efficient way to build up the aromatic core in one step.² The cyclone compound can be made by a double aldol condensation from benzil and diethyl 1,3-acetonedicarboxylate.³ Additionally, the versatility of this synthetic route and availability of many diaryl 1,2-diones and polycyclic ortho-quinones such as acenaphthenequinone and phenanthrenequinone allow an easy access to a wide range of substituted prehnitic dianhydrides.

Scheme II.1. Retrosynthetic analysis for the dianhydride monomer.

II.2.2. Synthesis of Diphenylprehnitic Dianhydride Monomer

Diphenylprehnitic dianhydride (**II-1**) was readily synthesized in three steps from diethyl 1,3-acetonedicarboxylate, benzil and diethyl acetylenedicarboxylate in high yields (Scheme II.2). The Diels-Alder reaction of bright orange-colored 2,5-dicarboethoxy-3,4-

diphenylcyclopentadienone (cyclone **II-2**), which was readily prepared by aldol condensation of benzil and diethyl 1,3-acetonedicarboxylate and diethyl acetylenedicarboxylate afforded the tetraester **II-3** in 95 % yield. Although hydrolysis of the tetraester can be done using either a base or an acid, it was found that acid hydrolysis with 48% HBr in acetic acid at reflux offers some advantages over the base hydrolysis (e.g., KOH in boiling ethylene glycol). These include a cleaner product, simple workup and better control of the reaction. Consequently, the formation of dianhydride **II-1** was accomplished upon thermal dehydration of diphenylprehnitic acid (**II-4**) by melting under vacuum. The resulting dianhydride was then recrystallized from chlorobenzene. The monomer obtained was of high purity and could be stored in a dry container over months without any deterioration. An alternative synthetic approach involved Diels-Alder reaction of **II-2** with inexpensive maleic anhydride, followed by aromatization with bromine to afford the monoanhydride-diester **II-5**. The hydrolysis of **II-5** gave the acid **II-4** which can be dehydrated to yield the final dianhydride product.

Scheme II.2. Synthetic routes to diphenylprehnitic dianhydride (II-1).

The hydrolysis of ethyl 5,6-diphenyl-1,2,3,4-benzenetetracarboxylate (**II-3**) under different conditions provided useful information on relative reactivity of the two different carbonyl groups. Even with 10 equivalents of potassium hydroxide in refluxing aqueous ethanol, the two esters at the 1,4-positions remained unreacted. The only product was the diacid-diester **II-6**. The ^{13}C NMR spectrum of the tetraester **II-2** showed two peaks at chemical shifts of 166.0 and 167.0 ppm, assigned to the two different carbonyl sp^2 carbons at C-1,4 and C-2,3 positions, respectively. Such a small difference in chemical shifts suggests that all four ester groups have similar reactivity towards a nucleophile, when only considering the electronic effect.⁴ The remarkable inertness of the ester group at the C-1 and C-4 positions towards nucleophilic attack during base hydrolysis, is obviously due to the steric hindrance provided by two pendant phenyl rings. Since both base hydrolysis and imide formation are reactions of nucleophilic displacement, the amine nucleophile used in polymerization should preferably attack the less hindered carbonyl groups at C-2 and C-3, rather than the two carbonyls adjacent to the phenyl groups.

II.2.3. Characterization of Diphenylprehnitic Dianhydride

The structure of dianhydride **II-1** was unambiguously confirmed by FTIR, ^1H and ^{13}C NMR and high-resolution mass spectrometry (HRMS). Two distinct peaks at 1855 and 1792 cm^{-1} corresponded to the symmetric and unsymmetric stretch of the carbonyl of the anhydride group. The aromatic protons in the ^1H NMR spectrum showed complicated splitting patterns the two pendant phenyl groups. It is difficult to assign for the different protons. The ^{13}C NMR spectrum clearly displayed the expected nine carbons. There were two carbonyl signals at 159.5 and 156.8 ppm for this unsymmetric dianhydride. The remaining seven signals in ^{13}C NMR spectrum were all in the aromatic region ranging from 127.7 to 150.3 ppm. The result from HRMS gave the absolute molar mass for the monomer, further confirming the structure.

The structural features of **II-2** have been further detailed by a single crystal X-ray diffraction analysis. The crystal structure (Figure II.3) shows that the prehnitic dianhydride group is almost planar. Dihedral angles (62.5° and 69.6°) between the pendant phenyl rings and the central aromatic core are considerably large when compared to that between two phenyls (49.8°), showing that three aromatic rings are highly twisted. The bulky phenyl groups push the two carbonyls at 1,4-positions away, causing a slight distortion of dianhydride rings. The length of the C(7)-C(8) bond ($1.495 \text{ \AA}$) is slightly longer than that of the C(9)-C(10) bond ($1.481 \text{ \AA}$), indicating that carbonyls at 2,3-positions of **II-1** should be slightly more reactive than the carbonyls at the 1,4-positions without considering the steric hindrance caused by the two phenyl rings. The bond angles of C(3)-C(10)-C(9) and C(10)-C(7)-C(8) are 133.4° and 108.0° , respectively. Both are off from the expected 120° , which suggests that the bent angle between the two anhydride groups is about 122° .

Figure II.3. Molecular structure of the dianhydride II-1 in its crystal form.

II.3. Polymer Synthesis

II.3.1. Model Reactions

Unlike PMDA and other commercially available dianhydrides, the polymerization of prehnitic dianhydride may present a potential problem associated with the formation of a monoimide at the 2,3-position. This would cause either incomplete polymerization or crosslinking. A model reaction of the dianhydride **II-1** with aniline was first carried out in *N*-methylpyrrolidinone (NMP) and gave a mixture of **II-7a**, **II-7b** and other unidentified compounds. When the same reaction was done in *m*-cresol, the desired diimide **II-7b** was obtained in quantitative yield (Scheme II.3). This solvent effect can be attributed to the fact that water is miscible with NMP but not with *m*-cresol, and the resulting water produced during the reaction in NMP can effectively interfere with imidization of the amic acid intermediate. A recent kinetic study on solution imidization suggests that both formation and cleavage of the amic acid are present and complete imidization occurs via relinking of partially degraded products and further cyclization of the reproduced amic acid are possible at 180 °C.⁵ However, prolonged heating at about 180 °C in NMP did not change the ratio of **II-7a** and **II-7b**.

Scheme II.3. Model reactions of the dianhydride **II-1** and aniline.

This model diimide **II-7b** was characterized by IR, ^1H and ^{13}C NMR and HRMS. The formation of imide was confirmed by IR. The two carbonyl bands at 1855 and 1792

cm⁻¹ for the anhydride group showed the typical shift to 1771 and 1730 cm⁻¹ for the imide. The ¹³C NMR spectrum showed two signals at 162.4 and 164.7 ppm corresponding to the carbonyl carbons and 13 signals in total corresponding to 13 chemically non-equivalent carbons. HRMS gave exactly the same mass as the one calculated for the molecular formula.

The structure of compound **II-7a** was confirmed by IR, ¹H and ¹³C NMR and MS. IR showed the imide carbonyl peaks at 1783 and 1720 cm⁻¹, plus a distinct carbonyl band at 1697 cm⁻¹ attributed to the carboxylic acid, and an OH band around 2550-3500 cm⁻¹. The NMR spectra proved the presence of aromatic protons and carbons in the molecule. Finally, MS measurement confirmed the molecular mass by showing a base peak at 418 (463-COOH), which is a common fragmentation for a carboxylic acid.

II.3.2. Polymer Synthesis and Structural Characterization

II.3.2a. Polymer Synthesis

On the basis of the results from the model reactions, one-step solution polymerizations of the dianhydride **II-1** with various aromatic diamines [**II-8(a-g)**] were best carried out in *m*-cresol in the presence of a small amount of isoquinoline at 200 °C (Scheme II.4). Water formed from imidization was removed together with a small amount of *m*-cresol with a stream of nitrogen. Depending on the diamine used, the solution concentration varied from 5% to 18% (wt/v). With rigid and/or linear diamines (e.g., *p*-phenylenediamine and 4,4'-oxydianiline), the solution concentration was kept low in order to prevent gel formation. For flexible or less linear diamines, especially for *m*-phenylenediamine, the solution concentration should be maintained as high as possible to suppress the formation of cyclic oligomers. High molecular weight poly(diphenyl prehnitimide)s **II-9(a-g)** were readily obtained from aromatic diamines in about 18 h.

Scheme II.4. Synthesis of poly(diphenyl prehnitimide)s **II-9(a-g)**.

II.3.2b. Structural Characterization

The structures of the synthesized polyimides were characterized by FTIR and high-field ^1H and ^{13}C NMR spectroscopy. By comparing IR spectra of the monomer **II-1**, model diimide **II-7b** and the polyimides synthesized, complete imidization during polymerization was confirmed (Figure II.4). The IR spectrum of dianhydride **II-1** displayed two carbonyl peaks at 1855 and 1792 cm^{-1} . For the model diimide, the two carbonyl peaks shifted to 1771 and 1730 cm^{-1} and the polymers showed there two peaks as well. The ^{13}C NMR spectrum of the polymer **II-9a** displayed two distinct signals at 162.4 and 164.7 ppm for the carbonyl carbons, which matched well with the two peaks in the spectrum of the structurally similar model diimide **II-7b** (Figure II.5).

Figure II.4. Comparison of IR spectra of monomer II-1, model diimide II-7b and polyimide II-9a.

Figure II.5. Comparison of ^{13}C NMR spectra of monomer II-1, model diimide II-7b and polyimide II-9a.

II.4. Properties of Poly(aryl prehnitimide)s

II.4.1. Solubility

As mentioned before, poly(aryl pyromellitimide)s derived from diphenylpyromellitic dianhydride and the rigid aromatic diamines like *p*-phenylenediamine and benzidine are highly insoluble and could not be prepared by a one-step solution polycondensation. In comparison, poly(aryl prehnitimide)s **II-9** show much improved solubility over poly(aryl pyromellitimide)s. With the exception of **II-9e**, polyimide **II-9** are readily soluble in many common organic solvents at ambient temperatures such as TCE, DMAc, NMP, DMSO, and DMF, *m*-cresol, and even pyridine (Table II.1). Polyimide **II-9b** is even readily soluble in chloroform and tetrahydrofuran (THF), presumably owing to its zigzag shape. It should be noted that high solubility in certain organic solvents (e.g., THF, DMF, and DMSO) which are miscible with water enables these polyimides to be fabricated easily as asymmetric membranes. Furthermore, the rod-like polyimide **II-9a** derived from *p*-phenylenediamine is remarkably soluble at ambient temperatures and can be readily produced in high molecular weight via a one-step polymerization process without precipitation or gelation. Evidently, the significant improvement in solubility for poly(aryl prehnitimide)s **II-9** is attributed to the unique bent diimide and twisted pendant phenyl groups. Although being soluble in *m*-cresol during polymerization, polymer **II-9e** could not be re-dissolved completely in the same solvent.

Table II.1. Solubilities of polymers **II-9**^a.

polymer II-9	CHCl ₃	TCE	DMF	DMSO	DMAc	NMP	<i>m</i> -cresol	THF	pyridine
a	-	+	+	+	+	+	+	-	+
b	+	+	+	+	+	+	+	+	+
c	-	+	+	+	+	+	+	-	+
d	±	+	+	+	+	+	+	-	+
e	-	-	-	-	-	-	±	-	-
f	±	+	+	+	+	+	+	-	+
g	-	+	+	+	+	+	+	-	+

^a Measured at room temperature with 5% (w/v). Key: +, soluble at room temperature; ±, partial soluble at room temperature; -, insoluble at room temperature.

II.4.2. Viscosity

Intrinsic viscosities of all polyimides **II-9(a-g)** ranged from 0.45 to 1.81 dL/g (Table II.2). The formation of creasable films from polymers **II-9(a-f)** indicates that these polyimides have reasonably high molecular weights and some degree of toughness. Polyimides **II-9(a-f)** appear to have relatively low solution viscosities and low molecular weights by GPC relative to polystyrenes, presumably due to the bent diimide structure. For example, polymers **II-9b** ($[\eta] = 0.50$ dL/g) and **II-9f** ($[\eta] = 0.77$ dL/g) had a number-average molecular weights of 21700 and 51000, respectively. In order to correlate the apparent molecular weight to solution viscosity for this type of polyimide, the relationship between absolute molecular weight, apparent molecular weight by GPC and solution viscosity need to be established. Thus, an end-capping polymerization was performed for polyimide **II-9b**. A small amount of 3,5-di-*tert*-butylaniline was used in the polycondensation of dianhydride **II-1** and diamine **II-8b**. The resulting polymer **II-10** (Figure II.6) was fractionated to exclude any linear or cyclic oligomers. It was labile to acid

and heat during isolation and purification. This end-capped polyimide had an intrinsic viscosity of 0.36 dL/g (NMP, 30 °C) and an absolute number-average molecular weight of 35000 determined by NMR analysis. In comparison, the apparent number-average molecular weight measured by GPC relative to polystyrenes was only about 9780, and much lower than the one measured by NMR. Therefore, the poly(aryl prehnitimide)s synthesized should have higher molecular weights than those determined by GPC.

Figure II.6. End-capped polyimide **II-10**.

Table II.2. Intrinsic viscosities of poly(aryl prehnitimide)s **II-9**.

Polymer II-9	$[\eta]^a$ (dL/g)	Film ^c
a	0.95	Clear, tough, flexible
b	0.50	Clear, tough, flexible
c	1.01	Clear, tough, flexible
d	1.81	Clear, tough, flexible
e	0.95 ^b	Brittle
f	0.77	Clear, tough, flexible
g	0.45	Clear, flexible

^a Intrinsic viscosity measured in NMP at 30 °C. ^b In *o*-chlorophenol at 30 °C. ^c Cast from TCE or *m*-cresol solution.

II.4.3. Thermal Properties

The thermal properties of polyimides **II-9(a-g)** were investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The glass transition temperatures (Tg's) of the polyimides measured by DSC and thermomechanical analysis (DMA) are summarized in Table II.3. In general, with increasing chain stiffness the detection of glass transitions by DSC becomes more difficult. Polyimides **II-9(b,c,d,e,f)** showed Tg's ranging from 362 to 437 °C (Figure II.7). The Tg's of polyimides **II-9(a,g)** were not detectable by DSC. It is known that the Tg's of poly(aryl pyromellitimide)s are also reported to be ill-defined and difficult to detect using DSC. The rigid structure of the prehnitimide and two pendant phenyl groups are responsible for high Tg values. The Tg's of polyimides **II-9** could also be determined by observing the maximum in the $\tan \delta$ values obtained from DMA measurements in stress-strain mode. A typical DMA trace from **II-9f** is shown in Figure II.8. Except for polyimides **II-9e** and **II-9g** that could not form tough films for DMA measurement, these polyimides had Tg's (max. $\tan \delta$) ranging from 340 to 443 °C. As expected, the highest Tg was obtained for the most rigid polyimide **II-9a**. The most flexible polyimide **II-9f** had the lowest Tg (340 °C). Increasing the chain stiffness or decreasing the number of bridging bonds in the diamines used shifted the Tg's to higher values, as seen for polymers **II-9e** (362 °C) and **II-9c** (402 °C). Polyimides **II-9a** and **II-9b** derived from phenylenediamines had Tg's over 440 °C.

Table II.3. Thermal properties of polymers II-9(a-g).

Polymer	T _g ^a (°C)	T _g (°C)	TGA ^d (°C)	TGA ^d (°C)
II-9	DSC	DMA	N ₂	air
a	N/O ^b	443	560	524
b	437	424	553	523
c	420	402	514	491
d	421	395	507	449
e	362	--- ^c	483	480
f	366	340	529	489
g	N/O	---	554	516

^a Except for II-9d measured by DSC at a heating rate of 10 °C/min, the rest were obtained from DSC in oscillation mode at a heating rate of 3 °C/min. ^b N/O: Not observed. ^c Films were not tough enough for DMA measurement. ^d 5% weight loss at a heating rate of 10 °C/min.

Figure II.7. DSC traces of polyimides II-9b, c, e, and f.

II-9f

Figure II.8. DMA diagram of polyimide II-9f.

Like many aromatic polyimides including poly(aryl pyromellitimide)s, all poly(aryl prehnitimide)s **II-9(a-g)** displayed excellent thermal stabilities. The onset temperatures for 5% weight loss in nitrogen were in the range of 483 to 560 °C, as assessed by TGA (Table II.3). In air these temperatures were lower, in the range of 449 to 524 °C. The excellent thermal stability of rigid rod-like polyimide **II-9a** was particular noteworthy, for its 5% weight loss at 560 °C in nitrogen and 524 °C in air. As shown in Figure II.9, the degradation for the uncapped polyimide **II-9b** began at about 485 °C in air and catastrophic decomposition appeared at about 555 °C. When being heated in air at 400 °C, this polymer lost 10% of its weight in about 14 h with a degradation rate of 0.0705 mg/h, then decomposed more rapidly at the rate of 0.196 mg/h. It should be mentioned that, since these polyimides are not end-capped and have different molecular weights, their molecular weights and the nature of the end group has a direct impact on thermal and thermooxidative stabilities.

II-9b

Figure II.9. Isothermal aging and TGA thermograms of polyimide **II-9b** (in air).

II.4.4. Mechanical Properties

The solvent-cast films for polymers II-9(a-e,f) were clear, flexible and tough. Young's moduli of these nonoriented, amorphous films were measured using DMA in tensile stress-strain mode. Loads were chosen such that a linear stress-strain relationship was obtained. Young's moduli (E') measured for polymers II-9(a-e,f) ranged from 2.07 GPa to 3.94 GPa (Table 3.4). High E' values (> 3.0 GPa) were observed for polymers II-9a, c and f. Polymer II-9b had a relatively low Young's modulus (2.07 GPa), probably due to its kink-like structure. In comparison, these poly(aryl prehnitimide)s appear to have a higher tensile moduli than PMDA-ODA polyimide. The tensile modulus of the latter nonoriented thin film has been reported to be 2.1 GPa.⁶ It should, however, be noted that different casting and DMA experiment conditions can vary the DMA data.

Table II.4. Young's moduli of polyimide II-9.

Polymer II-9	a	b	c	d	e	f	g
E' (GPa) ^a	3.14	2.07	3.94	2.85	--- ^b	3.14	---

^a Young's modulus measured from TMA. ^b Films were not tough enough for TMA measurement.

II.4.5. Dielectric Constants

The bent diimide structure may be more polar than the linear diimide of similar structure and as a result influence the dielectric constant of the resulting poly(aryl prehnitimide)s. It is therefore desirable to investigate the effect of the bent diimide functionality on the dielectric properties of these polyimides. The dielectric constants of polyimide II-9 were obtained by measuring dielectric relaxation.⁷ (Table II.5). The overall dielectric properties of polyimide II-9 are similar to the representative PMDA-ODA polyimide. The dielectric constants at ambient conditions range from 2.1 to 3.9. These

values compare to the dielectric constant of 3.5 at 1 KHz (at 25 °C) for the PMDA-ODA polyimide. It should be noted that the value of dielectric constants obtained by different methods might be quite different. Another method to measure the dielectric constants is to determine the relative permittivity (ϵ') by the procedure described in ASTM D-150-81. This method is more frequently used for determining the dielectric constants in industry.

Table II.5. Dielectric constants of polyimide II-9(a-e, g).

Polymer II-9	a	b	c	d	e	g
Dielectric constant ^a	3.52	3.90	2.15	2.54	2.13	3.56

^a measured at 1 KHz, 23 °C.

II.5. Conclusion

A series of high molecular weight, soluble polyimides have been synthesized from novel diphenylprehnitic dianhydride. Polyimides containing a bent prehnitimide structure possess improved solubility in common organic solvents. All polyimides synthesized have very high glass transition temperatures, excellent thermal stabilities, good mechanical properties and low dielectric constants.

II.6. Experimental

Materials. Bromine, *m*-Cresol, *o*-chlorophenol, isoquinoline, maleic anhydride and 4,4'-methylenedianiline (II-8d) were purchased from Aldrich Chemical Co. and used as received. 4,4'-Bis(4-aminophenoxy)biphenyl (II-8e), bis(4-aminophenoxy)diphenylsulfone (II-8f), and 9,9'-bis(4-aminophenyl)fluorene (II-8g) were received from New Seika Corp. and used without further purification. *m*-Phenylenediamine (II-8b) and *p*-phenylenediamine (II-8a) (Aldrich) were purified by

sublimation under vacuum. 4,4'-Oxydianiline (**II-8c**) (Aldrich) was recrystallized from ethanol. Other common organic solvents are reagent grade unless otherwise stated.

The cyclone II-2.

Benzil (63.0 g, 0.3 mol) and diethyl 1,3-acetonedicarboxylate (72.6 g, 0.36 mol) were dissolved in absolute methanol (600 mL) and the solution was cooled in ice. A methanolic solution of sodium hydroxide (12 g in 60 mL) was then slowly added with stirring below 10 °C. The mixture was stirred overnight at room temperature and yellow sodium salt (122.2 g) was filtered off. This salt (122.2 g) was mixed with acetic anhydride (300 mL) and to which was added conc. sulfuric acid dropwise till all goes into the solution. The solution became orange and stirred for 2 h. Water was then added dropwise to destroy excess acetic anhydride. Care was taken not to reach the temperature above 80 °C. Excess ice was added to precipitate the product which was stirred in water and filtered. After washing with water and drying in air, the product was recrystallized from high boiling cyclohexane: 101.2 g (89.7%). 122-123 °C (Lit.⁸ 121.8 °C).

The tetraester II-3.

Diethyl acetylenedicarboxylate (18.4 g, 10.8 mmol) was added to a solution of the cyclone II-2 (33.9 g, 90.2 mmol) in toluene (120 mL) at room temperature. The reaction mixture was heated at reflux overnight. After removal of toluene, the product II-3, was recrystallized from cyclohexane as white crystalline solids: 44.4 g (95%). m.p. 143-144 °C; ^1H NMR (400 MHz, CDCl_3) 7.12 (6 H, m), 6.95 (4 H, m), 4.34 (4 H, q, $J = 7.2$ Hz), 3.92 (4 H, q, $J = 6.8$ Hz), 1.34 (6 H, t, $J = 7.2$), 0.85 (6 H, t, $J = 7.2$); ^{13}C NMR (100 MHz, CDCl_3) 166.95, 165.96, 142.18, 136.92, 135.52, 130.37, 129.62, 127.56, 127.48, 62.26, 61.58, 13.85, 13.41. MS (EI, m/e , relative intensity %) 518 (M^{++} , 100).

Diphenylprehnitic Acid (II-4).

The tetraester II-3 (104 g) was dissolved in 350 mL of acetic acid in a 1 L round-bottomed flask equipped with a condenser, followed by addition of 140 mL of aqueous HBr solution (48%). The mixture was heated at reflux for 48 h. In about 24 h, some white

precipitates were formed, indicating the formation of the tetraacid. After the hydrolysis was complete, the reaction mixture was cooled to room temperature and the precipitate was collected by filtration. The filtrate was concentrated to yield more product **II-4**. After drying in air, diphenylprehnitic acid was obtained as white powders: 76.4 g (93.7%). ^1H NMR (200 MHz, DMSO-d_6) 7.11 (10 H, m); ^{13}C NMR (50 MHz, DMSO-d_6) 168.13, 167.82, 140.35, 137.20, 135.40, 130.43, 129.66, 127.45, 127.28. MS (EI, m/e, relative intensity %) 370 (M^+ , 100), caused by loss of 2 water from the parent molecular.

The diester diacid **II-4**.

The tetraester **II-3** (5.0 g) and KOH (10.8 g) were dissolved in 50 mL of water. The solution was refluxed for 12 h. After cooling to room temperature, conc. HCl (1.5 mL) was added into the solution. The white precipitates formed and collected by filtration. Washing with water twice and drying in air gave 4.3 g (96 %) of white powder product. ^1H NMR (200 MHz, DMSO-d_6) 7.65 (2H, s), 7.07 (10 H, m) 3.94 (4 H, q, $J = 7.10$ Hz), 0.82 (6 H, t, $J = 7.10$); ^{13}C NMR (50 MHz, DMSO-d_6) 167.32, 166.42, 140.93, 136.64, 134.56, 131.01, 129.45, 127.51, 122.97, 61.18, 13.26. MS (EI, m/e, relative intensity %) 444 (M^+ , 100), caused by loss of one water molecule.

The diester anhydride II-5.

The cyclone **II-2** (2.0 g) was mixed with 2.6 g of maleic anhydride in 8 mL of toluene in a 50 mL round-bottomed flask. The reaction mixture was heated at reflux for 5 h. After the solvent was evaporated using a rotary evaporator, the Diels-Alder adduct as a white powdered product was washed with diethyl ether and dried in air: 2.15 g (90.7%). This adduct (2.0 g) was dissolved in 2 mL of 1,2-dichlorobenzene in a 50 mL round-bottomed flask. To the solution was added 0.46 mL (1.43 g) of Br₂. The mixture was then gently heated up to reflux for 5 h and cooled down to room temperature. The product crystallized on standing at room temperature overnight was collected by filtration and washed with hexane and dried in air: 1.55 g (77.9%). m.p. 182-183 °C; IR (KBr, C=O) 1849, 1784, 1732 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) 7.18 (6 H, m), 7.00 (4 H, m), 4.18 (4 H, q, J = 7.2 Hz), 1.05 (6 H, q, J = 7.2 Hz); ¹³C NMR (50 MHz, CDCl₃) 164.02, 160.20, 147.61, 135.14, 133.70, 129.43, 128.48, 127.97, 112.26, 62.64, 13.60. MS (EI, m/e, relative intensity %) 444 (M⁺, 100).

Diphenylprehnitic dianhydride (II-1).

A 250 mL, round-bottomed flask containing the crude tetraacid (63.8 g) was placed in an aluminum block preheated at 320 °C. After the tetraacid completely melted, the melt was kept under vacuum (via a water pump) at the melting temperature for 1 h. The product in the flask was cooled to room temperature, and recrystallized from chlorobenzene (100 mL). The yellowish dianhydride was dried under high vacuum (5 mmHg) at 210 °C for 2 days, and stored in a desiccator over P₂O₅. The yield was 49.8 g (84.3%). m.p. 255-256 °C; IR (KBr, C=O) 1847.1, 1784.2 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 7.34 (6 H, m), 7.06 (4 H, m); ¹³C NMR (100 MHz, CDCl₃) 159.5, 156.8, 150.3, 135.1, 131.2, 129.7, 129.4, 128.3, 127.7; HRMS: calcd for C₂₂H₁₀O₆, 370.0467; found 370.0467.

N,N-diphenyldiphenylprehnitimide (II-7b) (Model diimide).

Diphenylprehnitic dianhydride (0.7406 g, 2.000 mmol) and freshly distilled aniline (0.4470 g, 4.800 mmol) were dissolved in 12 mL of *m*-cresol containing 5 drops of

isoquinoline. Under a stream of nitrogen, the mixture was heated up to 200 °C and kept at the same temperature overnight. Most of solvent was then distilled off. The slightly dark product was washed with diethyl ether and recrystallized from toluene. The yield of **II-7b** was 0.94 g (90 %). m.p. 290.0-290.5 °C; IR (KBr, C=O) 1771 and 1730 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 7.42 (m, 10 H), 7.25 (m, 6 H), 7.10 (m, 4 H); ¹³C NMR (100 MHz, CDCl₃) 164.94, 162.44, 147.15, 133.60, 133.13, 131.19, 129.64, 129.03, 128.85, 128.52, 128.46, 127.93, 127.71, 126.58; HRMS: calcd for C₃₄H₂₀N₂O₄, 520.1424; found 520.1402.

Typical Procedure for Polymerization.

To a 100 mL three-neck, round-bottomed flask were added dianhydride **II-1** (1.4813 g, 4.000 mmol), freshly sublimed *p*-phenylenediamine (**II-8a**) (0.4326 g, 4.000 mmol), *m*-cresol (48 mL), and isoquinoline (10 drops). The reaction mixture was heated to 90 °C and held at this temperature for 2 h, then the temperature was elevated to 220 °C (oil bath temperature) under nitrogen. The reaction continued for 18 h and during this period of time about 10 mL of *m*-cresol was distilled off. The reaction solution was cooled to about 100 °C and poured into methanol (400 mL). The yellowish polymer was collected by filtration and washed with methanol using a Soxhlet extractor overnight. After drying under high vacuum (5 mmHg) at 150-200 °C, polyimide **II-9a** was obtained as yellow powders: 1.53 g (86%).

End-capped polymer **II-10**.

In a 100 mL, three-neck, round-bottomed flask were added dianhydride **II-1** (1.9000 g, 5.1307 mmol), freshly sublimed *m*-phenylenediamine (**II-8b**) (0.5493 g, 5.0799 mmol), 3,5-di-*tert*-butylaniline (0.0209 g, 0.1016 mmol), *m*-cresol (19 mL), and isoquinoline (5 drops). The reaction mixture was heated to 220 °C under nitrogen and held at this temperature for 24 h. During the course of the reaction, 10 mL of *m*-cresol was

distilled off. The viscous solution was cooled to room temperature and diluted with chloroform (10 mL). The polymer was then precipitated into methanol (400 mL) and collected by filtration. After washing with methanol and drying in air, the polymer was re-dissolved in chloroform (120 mL), and to which methanol (about 40 mL) was added to precipitate the polymer. The gummy precipitate was dissolved in chloroform (20 mL) and precipitated into methanol (200 mL). After filtration and drying under high vacuum (5 mmHg) at room temperature overnight, polymer **II-10** was obtained as yellow powders: 1.55 g (69%). $[\eta] = 0.36$ dL/g (NMP, 30 °C); $M_n = 35000$ (by NMR), $M_n = 9780$, $M_w/M_n = 1.80$ (by GPC).

Film casting.

All polymer films were cast from 1,1,2,2-tetrachloroethane (TCE) solution. A typical procedure for film casting is as follows: The purified and dried polymer (100-200 mg) was dissolved in 2-4 mL of TCE. The solution was then transferred by pipette-filtration into a cylindrical glass mould (diameter = 40 cm, height = 25 cm, thickness = 2 cm) placed on a glass plate. The mould was covered with a glass plate. An orifice at the top edge of the mould allowed the solvent to evaporate slowly at room temperatures for the period of 3-5 days. The film was removed from the glass mould by adding water to peel off the film. The circular and clear films were then placed in a vacuum oven (5 mmHg). The oven temperature was initially at 80 °C for 24 h, then gradually raised to 150 °C and held at this temperature for two weeks.

Characterization.

The ^1H and ^{13}C NMR spectra were recorded on either a Varian Gemini-200 or a Bruker-400 instruments using tetramethylsilane as an internal reference. Infrared measurements were performed on a Perkin-Elmer 1600 or a Bomem Michelson 120 FTIR spectrometer. Low-resolution mass spectra were obtained on a Du Pont 21-492B

spectrometer. The apparent molecular weights of the polymers were determined by gel permeation chromatography (GPC) using chloroform at ambient temperature. Molecular weight calculations were based on polystyrene standards. A PL-Gel column (1.0 x 30 cm, 5 micron) with a chloroform elution rate of 1.0 mL/min was used. Elution of the polymers from the column was detected by a Perkin-Elmer UV-vis spectrophotometric detector set at 254 nm. Intrinsic viscosities were measured in N-methyl-2-pyrrolidinone or o-chlorophenol solution at 30 °C using an Ubbelohde dilution viscometer. The glass transition temperatures (T_g's) were determined on a Seiko 220C differential scanning calorimeter with a heating rate of 3 °C/min in oscillation mode under nitrogen (50 mL/min), taken as the midpoint of the change in slope of the baseline. Thermal and thermo-oxidative stabilities of the polymer samples were determined using a Seiko 120 TG/DTA analyzer run from 25 °C to 700 °C or 1000 °C at a heating rate of 10 °C/min. Isothermal aging tests were conducted in air at a fixed temperature of 400 °C for 25 h. The tensile mechanical properties of the polymer films were measured using a Seiko 120C TMA/SS analyzer run in stress-strain mode. A stamp was used to cut out a film strip (length = 10 mm, width = 2 mm, thickness = 0.025-0.125 mm) which was mounted between two chucks in the TMA/SS instrument. These films were tested by measuring the stress and strain while applying a linear load program. For Young's modulus at 25 °C, the parameters were set as: offset load = 20 g, load amplitude = 10 g and cycling frequency = 0.05 Hz. Young's moduli were obtained from the slope of the linear portion of the stress-strain plots (E'). After the data were collected, the same film was used without changing the parameters to Young's modulus variation with temperature by heating to 450-500 °C at a ramp rate of 3 °C/min in static air. Dielectric relaxation measurement was undertaken on a Hewlett Packard HP4284A impedance analyzer. The measurement was done in the Department of Materials Science and Engineering at McMaster University.

The crystal structure determination was performed at the Department of Chemistry, University of Ottawa, Ottawa, Canada. The single crystal of II-1 was grown in prism by

condensation of the vapor of during sublimation at 200 °C under high vacuum (5 mmHg) and cut with dimensions of 0.2 x 0.2 x 0.2 mm. All measurements were made on a Rigaku diffractometer with Mo K α radiation. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement using the setting angles of 25 reflections in the range $40 < 2\theta < 50$ corresponded to a triclinic cell with dimensions $a = 12.826$ (3) Å, $b = 13.188$ (3) Å, $c = 12.473$ (4) Å, $\alpha = 110.242$ (21)°, $\beta = 113.420$ (22)°, and $\gamma = 67.645$ (18)°. For $Z = 4$ and $FW = 370.31$, the calculated density is 1.411 g/cm³. Based on the systematic absences, the space group was determined to be $P1$. The data were collected at 22 °C using the $\omega - 2\theta$ scan technique to a maximum 2θ value of 49.9. The residuals are as follows: for significant reflections, $R_f = 0.131$ and $R_w = 0.031$. A total of 6388 reflections was collected. The unique set contains only 6085 reflections. The standards were measured after every 150 reflections. No crystal decay was notice. The data were collected for Lorentz and polarization effects. No absorption correction was made. The structure was solved by direct methods. There are two molecules per asymmetric unit. All the phenyl groups were refined as rigid groups to increase the ratio reflections/parameters. All the atoms were refined anisotropically except the hydrogen. The hydrogen atoms were calculated assuming a distance C-H of 1.007 Å. Calculations were performed using the NRCVAX crystallographic software package.

References

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1. Suzuki, S.; Kaneda, I.; Takahashi, M.; Nagai, H. *Jpn Patent* 71 16 906, May 10, 1971, *Chem. Abstr.* 75:141,367k.
  2. Harris, F. W.; Hsu, S. L. C. *High Perf. Polym.* **1989**, *1*, 3.
  3. White, D. W. *J. Org. Chem.* **1974**, *39*, 1951.
  4. Ando, S., Matsuura, T., Sasaki, S. *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 2285.
  5. Kim, Y. J.; Glass, T. E.; Lyle, G. D.; McGrath, J. E. *Macromolecules* **1993**, *26*, 1344.
  6. Mita, I.; Kochi, K.; Hasegawa, M.; Iizaka, T.; Soma, H.; Yokota, Y.; Horiuchi, in *Polyimides: Materials, Chemistry and Characterization*, Feger, C., Khojasteh, M., McGrath, J., Eds., Elsevier: Amsterdam, 1989, pp 1.
  7. Zaluski, C.; Xu, G.; Qi, Y.; Wang, Z. Y. *J. Polym. Sci. Part B, Polym. Phys.* **1996**, *34*, 731.
  8. The procedure for the preparation of compound II-2 was kindly provided by W. A. Feld, Chemistry Department, Wright State University, Dayton, OH 45435.

CHAPTER III. COPOLYIMIDES CONTAINING A PREHNITIMIDE UNIT

Besides the structural modification of diamine and dianhydride monomers, copolymerization of two different dianhydrides or two different diamines is another common practice to improve the solubility and achieve a combination of desired properties.¹ As stated in Chapter I, regardless the flexible linkages cause the decrease in high temperature properties of the rigid polyimides, in fact, it is difficult to achieve a high content (ca. over 50%) of pyromellitimide by direct solution copolymerization of pyromellitic dianhydride (PMDA) and another dianhydride monomer even with flexible diamine such as 4,4'-oxydianiline or 4,4'-methylenedianiline.¹ We have demonstrated that the bent dianhydride, diphenylprehnitic dianhydride, could be successfully synthesized and polymerized with an aromatic diamine by one-step solution polycondensation. The resulting polyimides, even derived from a rigid diamine (e.g. *p*-phenylenediamine), are highly soluble in common organic solvents. Therefore, it is advantageous to use this bent dianhydride as the second monomer to copolymerize with PMDA and *p*-phenylenediamine by solution polymerization. The resulting copolyimide should have improved solubility due to the bent diimide structure yet, still maintain high temperature properties.

III.1. Copolymerization by Random and Sequential Addition

The synthesis of the random copolyimide with 1:1 mole ratio of diphenylprehnitic dianhydride and PMDA with 2 mole equiv. of *p*-phenylenediamine was first attempted using solution polycondensation in *m*-cresol at high temperature (200 °C). Although the concentration of the reaction solution was very dilute (2%), this copolyimide was still precipitated out during the polymerization. This is probably because PMDA is more reactive than diphenylprehnitic dianhydride, and the insoluble oligopyromellitimide blocks are formed first. However, when less reactive, but more soluble diphenylprehnitic

dianhydride was added first, followed by PMDA, the nearly alternating copolyimide (**III-1a**) with 1:1 mole ratio of diphenylprehnitic dianhydride and PMDA was obtained in high molecular weight. The polymer solution remained clear and very viscous with a 2% concentration during polymerization. The copolymer could form flexible transparent film cast directly from the reaction solution (*m*-cresol), and had an intrinsic viscosity of 2.30 g/dL in *m*-cresol at 30 °C. When using diphenylprehnitic dianhydride and PMDA in a 2:1 ratio by sequential addition with 2% solid content in *m*-cresol, high copolymer (**III-1b**) ($[\eta] = 2.80$ dL/g in NMP) was readily obtained (Figure III.1).

Figure III.1. Copolyimides **III-1a** (X:Y = 1:1) and **III-1b** (X:Y = 1:2).

Copolyimide **III-1a** remained soluble in *m*-cresol during polymerization, but the isolated copolymer was not soluble in TCE, DMAc, or NMP. With increase of the prehnitimide content, the solubility of the resultant copolyimide (**III-1b**) increased sharply. Table III.1 showed the solubility of these two copolyimides.

Table III.1. Solubilities of polyimides **III-1a** and **III-1b**^a.

Polymer	CHCl ₃	TCE	DMF	DMAc	DMSO	NMP	<i>m</i> -Cresol	THF	Pyridine
III-1a	-	-	-	-	-	-	+	-	-
III-1b	-	-	+	+	+	+	+	-	-

^aMeasured at room temperature with 5 % (w/v). Keys: +, fully soluble; -, insoluble.

III.2. Perfectly Alternating Copolyimides

Obviously, this sequential copolymerization could not produce the alternating copolyimide without a defect or short block. It is therefore appropriate to further investigate the effects of the absolute alternating structure that the bent prehnitimide unit that would have on the solubility of rigid copolyimides. Two perfectly alternating copolyimides were prepared from the diamine monomer **III-2**, which was derived from diphenylprehnitic dianhydride (**II-1**) and *p*-phenylenediamine, PMDA and 1,4,5,8-naphthalenetetracarboxylic dianhydride (NDA) (Figure III.2).

Figure III.2. Dianhydrides and the diamine **III-2** for perfectly alternating copolyimides.

III.2.1. Synthesis of Diamine Monomer Containing a Prehnitimide Unit

The red-colored diamine **III-2** was synthesized by reduction of the dinitro precursor derived from **II-1** and 4-nitroaniline. The reduction could be done in moderate to high yields by hydrogenation with the PtO_2 catalyst. The diamine monomer was fully characterized by spectroscopic means and chemical analysis. The IR spectrum confirmed the presence of the carbonyl groups of the imide (1770 and 1722 cm^{-1}). By comparing the IR spectra of the dinitro compound and the diamine, the disappearance of the nitro peaks at 1347 and 1523 cm^{-1} in the diamine spectrum, and the appearance of two peaks at 3485 and 3381 cm^{-1} indicated the formation of a primary amine. The formation of an amine can also be confirmed by comparing the ^1H NMR spectra of the dinitro compound and the diamine.

The former spectrum showed two doublets at 8.31 and 7.74 ppm corresponding to the aromatic protons. These two doublets shifted to higher field in the ^1H NMR spectrum of the diamine (6.62 and 5.39 ppm). The ^{13}C NMR spectrum of **III-2** showed the total of the 13 magnetically non-equivalent carbons including the two carbonyl carbons. The elemental analysis further confirmed the molecular formula of this diamine monomer.

III.2.2. Synthesis of Perfectly Alternating Copolyimides

Polymerizations of diamine **III-2** with PMDA and NDA, respectively, were carried out in *m*-cresol in the presence of a small amount of isoquinoline at 200 °C. The solution concentration was best kept at 2% in order to prevent the gelation. The resulting polyimides **III-3** and **III-4** (Figure III.3) remained in solution during the course of polymerization.

Figure III.3. Alternating copolyimides **III-3** and **III-4**.

The alternating diad structures of copolyimides **III-3** and **III-4** were confirmed by IR and NMR spectra. To assist the characterization, three model bisimides **III-5,6,7** representing all three possible diads were prepared from *p*-phenylenediamine, phthalic anhydride, and 1,8-naphthalic anhydride. Two characteristic carbonyl bands were observed for copolyimide **III-3** at 1730 and 1776 cm^{-1} in IR. Four carbonyl bands were found in the region of 1680-1775 cm^{-1} for **III-4**. Model imides **III-5,6,7** also showed those carbonyl bands in the same region. The ^1H NMR spectrum of polymer **III-4** displayed two aromatic protons Ha and Hb from the *p*-phenylene moiety at 7.72 and 7.50 ppm. By comparing 2D-

HETCOR spectra of model bisimides **III-5,6,7**, Ha and Hb were assigned to the protons adjacent to the prehnitimido unit (at 7.72 ppm) and naphthalimido unit (at 7.50 ppm), respectively (spectrum a, Figure 4.3) For comparison, the corresponding two protons in bisimide **III-5** also appeared at 7.64 and 7.43 ppm (spectrum b, Figure III.4). On the other hand, the same protons for the homopolyimide **II-9a** derived from diphenylprehnitic dianhydride (**II-1**) and *p*-phenylenediamine appeared as a singlet at 7.62 ppm, matching well to the corresponding proton peak of bisphthalimide **III-6** (7.59 ppm, spectra c and d). Furthermore, the phenylene protons of bisnaphthalimide **III-7** showed as a singlet at 7.47 ppm (spectrum e). In addition to the above corroborative data, the absence of two singlet at 7.47 and 7.59 ppm in the spectrum (a) due to two symmetrical diads further proved the alternating structure of **III-4**.

Figure III.4. ^1H NMR (400 MHz, TCE-d_2) spectra of (a) copolyimide **III-4**, (b) bisimide **III-5**, (c) poly(p-phenylene diphenylprehnitimide) **II-9a**, (d) bisphthalimide **III-6**, and (e) bisnaphthalimide **III-7**.

Intrinsic viscosity of the “as-prepared” polyimides **III-3** and **III-4** were 0.57 and 0.89 dL/g, respectively (Table 4.2). Creasible tough films could be cast from the reaction solution for both polymers, indicating the formation of high molecular weight polymers. Thermogravimetry (TG) of both “as-prepared” polyimides showed the loss of water occurring at 280-300 °C. After being treated at 300 °C for a short time (10 min) to effect complete imidization, the powdered copolyimides showed no weight loss up to 450 °C. As expected, solution viscosities increased to 1.04 and 1.20 dL/g for **III-3** and **III-4**, respectively.

Table III.2. Intrinsic viscosity of copolyimides **III-3** and **III-4**.

Polymer	III-3	III-3 (cured) ^a	III-4	III-4 (cured)
[η] (dL/g) ^b	0.57	1.04	0.89	1.20

^a Powdered “as-prepared” polyimides were heated at 300 °C for 10 min. ^b Intrinsic viscosity in NMP at 30 °C.

III.2.3 Properties of Alternating Copolyimides

III.2.3a. Solubility

Alternating copolyimides **III-3** and **III-4** were remarkably soluble in organic solvents like DMF, DMAc, NMP, and *m*-cresol (Table III.3). The significant improvement in solubility, as compared to the copolyimide produced by sequential copolymerization, is evidently attributed to the bent prehnitimide unit and the perfect alternate sequence. Regular insertion of the bent unit into the rigid-rod backbone effectively prevents the polymer chains from close packing or strong interchain interaction, thus allowing them to be solvated and dissolved. The pendant phenyl rings attached to the central benzene core also contribute to the diminution of strong interchain interaction to some extent. It is worthy to note that polyimide **III-4** containing the naphthalimide moiety was more soluble than **III-3**

in TCE. It was also noticed that the polymers became slightly less soluble after being thermally treated in the solid powder form. The minor decrease in solubility was primarily due to the completion of imidization, rather than the increase in crystallinity or cross-linking. Wide-angle X-ray diffractograms of "as-prepared" **III-4** showed a low degree of crystallinity. There was no sign of distinct higher order for the thermally treated **III-4** (Figure III.5). Polymer **III-3** had similar wide-angle X-ray diffractograms.

Table III.3. Solubility of copolyimide **III-3** and **III-4**.

Polymer	Solubility ^a					
	TCE	DMF	DMAc	NMP	<i>m</i> -cresol	pyridine
III-3 -	+	+	+	+	+	
III-3 (cured)	-	+	±	+	+	±
III-4 +	+	+	+	+	+	
III-4 (cured)	+	+	+	+	+	±

^a Room temperature, 5% (w/v), Key: +, fully soluble, ±, partially soluble; -, insoluble.

Polyimide **III-4**

Figure III.5. Wide-angle X-ray diffractograms of (a) "as-prepared" **III-4**, and (b) thermally treated **III-4**.

III.2.3b. Thermal and Mechanical Properties

Copolyimides **III-3** and **III-4** displayed good thermal stability, as assessed by TG. The onset temperatures for 5% weight loss in nitrogen were 530 °C for both polyimides after thermal treatment. The “as-prepared” polyimides degraded easily in air, for the 5% weight loss occurring at 365 °C and 403 °C for **III-3** and **III-4**, respectively (Table III.4). Neither the glass transition temperatures nor the crystalline melting endotherms was detected for these two polyimides by DSC. Young’s moduli determined by TMA for both “as-prepared” polymers were in the vicinity of 3 GPa. After thermal treatment at 300 °C for 10 min, Young’s modulus of polymer **III-4** dropped from 3.3 to 1.6 GPa. The decrease of Young’s modulus is indicative of the increased stiffness of the polymer backbone as a result of further thermal imidization.

Table III.4. Thermal stability of polyimide **III-3** and **III-4**.

Polymer	III-3	III-3 (cured)	III-4	III-4 (cured)
Td (°C) in N ₂ ^a	365	530	505	530
Td (°C) in air ^a	356	424	403	416

^a Onset temperature for 5% weight loss, obtained on a Seiko TG 220, at a heating rate of 10 °C/min.

III.3. Conclusion

Alternate insertion of a bent unit into the rigid-rod polyimide is an effective way to break the linear rod-like regularity and improve the solubility, as demonstrated by synthesizing soluble rigid polyimides **III-3** and **III-4**.

III.4. Experimental

Materials.

4-nitroaniline was purchased from Aldrich Chemical Co. and used as received. Pyromellitic dianhydride (PMDA) was purchased from Allco Chemical Corporation and heated in a oven at 100 °C before used. 1,4,5,8-Naphthalenetetracarboxylic dianhydride (NDA) (Aldrich) was purified by recrystallization from DMSO. Other chemicals and solvents have been mentioned in Chapter II and therefore are omitted in this section.

The diamine III-2.

The solution of diphenylprehnitic dianhydride (17.0 g, 45.9 mmol) and 4-nitroaniline (15.8 g, 114.9 mmol) in *m*-cresol (30 mL) and isoquinoline (15 drops) was stirred under nitrogen at 170 °C for 6 h and then poured into 200 mL of 95% ethanol. The dinitro product was filtered and dried in air: 19.5 g (69.6%); mp 314 °C (DSC); IR (KBr, C=O), 1779, 1735 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 8.31 (4H, d, J = 9.08 Hz), 7.74 (4H, d, J = 9.08 Hz), 7.30 (6 H, m), 7.09 (4 H, m); ¹³C NMR (100 MHz, CDCl₃) 163.96, 161.59, 148.24, 146.79, 136.74, 133.47, 132.61, 129.47, 128.96, 127.93, 127.65, 126.61, 124.38.

The above dinitro compound (5.0g) in tetrahydrofuran (45 mL) and 95% ethanol (20 mL) was reduced using PtO₂ (0.1 g) in a hydrogenation apparatus under 50 psi of hydrogen for 8 h at room temperature. After removal of the catalyst and solvents, diamine

III-2 was recrystallized from acetonitrile and dried in a vacuum oven (5 mmHg) at 150 °C overnight: 3.6 g (80%). mp 575 °C (DSC); IR (KBr, C=O) 1770, 1722 cm⁻¹; ¹H NMR (400 MHz, DMSO-d₆) 7.16 (10 H, m); 7.00 (4 H, d, J = 8.60 Hz); 6.62 (4 H, d, J = 8.60 Hz); 5.39 (4 H, s); ¹³C NMR (100 MHz, DMSO-d₆) 165.33, 163.01, 148.83, 144.73, 133.82, 133.39, 129.67, 128.10, 127.64, 127.43, 127.07, 119.31, 113.39. Anal. calcd for C₃₄H₂₂N₄O₄: C 74.17%, H 4.03%, N 10.18%; found: C 74.11%, H 3.92%, N 10.01%.

Synthesis of Model bisimide **III-5**.

The solution of phthalic anhydride (4.0 g, 27.0 mmol) and 4-nitroaniline (4.10 g, 29.70 mmol) in *m*-cresol (10 mL) and isoquinoline (5 drops) was stirred under nitrogen at 170 °C for 6 h and then poured into 200 mL of 95% ethanol. The nitro product was filtered and dried in air: 4.8 g (60.0%).

This nitro compound (1.0 g, 3.7 mmol) was then reduced by refluxing in tetrahydrofuran (60 mL) and 95% ethanol (10 mL) with iron powder (4.2 g, 20 mmol) and 10 drops of concentrated hydrochloric acid for 9 h. After filtration, the filtrate was concentrated in vacuo to yield N-(4-aminophenyl)phthalimide which was washed with hot methanol and dried in an oven at 100 °C overnight: 0.66 g (75%); mp 243 °C (DSC).

N-(4-aminophenyl)phthalimide (0.30 g, 1.26 mmol) and 1,8-naphthalic anhydride (0.23 g, 1.15 mmol) were dissolved in 5 mL of *m*-cresol containing isoquinoline (5 drops). The mixture was stirred under nitrogen at 170 °C for 6 h. The solution was dropped into 50 mL of 95% ethanol. By filtration, the product was collected and recrystallized from 1,2-dichlorobenzene to give diimide **III-5**: 0.35 g (74.4 %); mp 344 °C (DSC); IR (KBr, C=O) 1779, 1720, 1705, 1668, cm⁻¹; MS (EI, m/e, relative intensity %) 418 (M⁺, 89).

Model bisimides **III-6** and **III-7**.

These two bisimides were synthesized by heating *p*-phenylenediamine (1.0 g) with phthalic anhydride (3.0 g) and 1,8-naphthalic anhydride (4.0 g) in 1-cyclohexyl-2-pyrrolidinone (25 mL) at 200 °C for 4 h, respectively. The solution was allowed to cool to room temperature. The solid products precipitated from the solution, and was collected by filtration. The products was washed several times with methanol and dried in an oven at 150 °C overnight. **III-6**: mp 370 °C (DSC); IR (KBr, C=O) 1702, 1779 cm⁻¹; MS (EI, m/e, relative intensity %) 368 (M⁺, 100). **III-7**: mp 332 °C (DSC); IR (KBr, C=O) 1705, 1665 cm⁻¹; MS (EI, m/e, relative intensity %) 468 (M⁺, 58).

Typical Procedure for Polymerization.

To a 100 mL three-neck, round-bottomed flask were added PMDA (0.6544 g, 3.000 mmol), the diamine **III-2** (1.6519 g, 3.000 mmol), *m*-cresol (60 mL), and

isoquinoline (10 drops). The reaction mixture was heated to 90 °C and held at this temperature for 2 h, then the temperature was elevated to 220 °C (oil bath temperature) under nitrogen. The reaction continued for 18 h and during this period of time about 10 mL of *m*-cresol was distilled off. The reaction solution was cooled to about 100 °C. The polymer was precipitated into methanol (400 mL) and collected by filtration. The polymer in light brown colour was further washed with methanol using a Soxhlet extractor overnight. After drying under high vacuum (5 mmHg) at 150-200 °C, polyimide **III-3** was obtained as brown powders: 1.96 g (89%).

Copolymer **III-1a**.

A three-neck 250 mL round-bottomed flask was equipped with two 100 mL dropping funnels and a magnetic stirrer. The whole set was kept under nitrogen. To the flask were added 0.6488 g (6.000 mmol) of *p*-phenylenediamine, 32 mL of *m*-cresol and 10 drops of isoquinoline. PMDA (0.6544g, 3.000 mmol) was dissolved in 23 mL of *m*-cresol in a dropping funnel, and diphenylprehnitic dianhydride (**II-1**) (1.1110 g, 3.000 mmol) was dissolved in 45 mL of *m*-cresol in another dropping funnel. After the flask was heated to 210 °C (oil bath), the solution of diphenylprehnitic dianhydride was added into the flask at a rate of 40 drops per 10 min at the beginning for 40 min and at a rate of 10 drops per 10 min afterward. After the completion of addition, the reaction mixture was stirred at 210 °C for 1 h. Then the addition of PMDA started with a rate of 20 drops per 10 min until the half of the PMDA solution was added and continued at a rate of 5 drops per 10 min afterward. A small amount of *m*-cresol (5 mL) was added twice to each dropping funnel to wash the residual starting dianhydrides into the reaction flask. The polymerization reaction was continued for 24 h. During the course of reaction, about 30 mL of *m*-cresol was distilled off. The viscous polymer solution was then poured into 500 mL of methanol. The polymer was collected by filtration and washed with boiling methanol for several times, then dried in a vacuum oven (5 mmHg) at 150 °C for 2 days: 2.09 g (95.2 %).

Copolymer III-1b.

p-Phenylenediamine (0.8111 g, 7.5000 mmol), **II-1** (1.8516 g, 5.0000 mmol), *m*-cresol (80 mL) and 10 drops of isoquinoline were placed in a 250 mL, three-neck round-bottomed flask equipped with a magnetic stirrer and a 100 mL dropping funnel containing 0.5454 g of PMDA in 60 mL of *m*-cresol. The reaction mixture was heated to 210 °C (oil bath) under a stream of nitrogen. The PMDA solution was then added into the flask over 1 h. About 20 mL of *m*-cresol was used twice to wash the residual PMDA funnel into the flask. The reaction solution became viscous immediately after the completion of addition of PMDA. The reaction was carried out for 48 h and 50 mL of *m*-cresol was distilled off. The hot reaction solution was poured into 500 mL of methanol and the resultant polymer was collected by filtration. After washing with boiling methanol for several times and drying in a vacuum oven (5 mmHg) at 150 °C for 2 days, the copolymer **III-1b** was obtained: 2.62 g (89.1 %).

References

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1. Harris, F. W.; Lanier, L. H. In *Structure-Solubility Relationships in Polymers*, Harris, F. W.; Seymour, R. B. Eds., Academic Press: New York, 1977, pp183.

CHAPTER IV. [5]HELICENE-BASED AB-TYPE POLYIMIDES

IV.1. Introduction

IV.1.1. AB-Type Polyimides

To date, most condensation polyimides such as Du Pont's Kapton® have been synthesized by polymerization of two difunctional monomers: a dianhydride and a diamine. Accordingly, much effort has been directed towards the design and preparation of new dianhydrides and diamines. Unlike many condensation polymers that can be made from a bifunctional monomer, very few aminoanhydride monomers and their corresponding AB-type polyimides are known and well characterized. This result is mainly attributed to the ease of self condensation between the amine and anhydride groups. Two known aminoanhydrides, 4-aminophthalic anhydride¹ and 4-aminonaphthalic anhydride² (Figure IV.1), were obtained by reduction of the corresponding nitro precursors. It is difficult to isolate the former as a pure monomer due to rapid oligomerization during drying or heating prior to melting. As a result, 4-aminophthalic anhydride and its many derivatives are difficult to polymerize to high molecular weight.^{1,3} 4-Aminonaphthalic anhydride was stable during isolation than 4-aminophthalic anhydride, but polycondensation of this aminoanhydride is likely to lead to the formation of an insoluble rigid-rod polyimide.

4-aminophthalic
anhydride

4-aminonaphthalic
anhydride

Figure IV.1. Structures of known aminoanhydrides.

As mentioned in Chapter I, only a few known AB-type polyimides have been made from either an amino-dicarboxylic acid (A, Figure IV.2) via a “phosphonylation”⁴ or a mono-ester of amino-dicarboxylic acid (B, Figure IV.2) by a direct polycondensation.⁵ Both of these two monomers can be isolated and purified as monomers because they are more stable than the corresponding aminoanhydrides. High molecular weight AB polyimides have been synthesized from these two monomers via poly(amic acid)s. The polyimide derived from monomer B was soluble in polar organic solvents. However, direct polymerization of the amino-diester C (Figure IV.2) in *m*-cresol or neat could only afford a low molecular weight polyimide with an inherent viscosity of 0.13 dL/g,⁶ presumably because of the low reactivity of the diester group.

Figure IV.2. AB-type monomers for polyimides.

From a synthetic point of view, using an AB monomer can avoid the strict stoichiometric control needed in polycondensation, offering obvious advantages in the production and processing of polyimides. In the conventional practice of making polyimides derived from a dianhydride and a diamine monomer, it is necessary to weigh the two monomers precisely with a 1:1 mole ratio in order to obtain a high molecular weight polymer. Also, a dianhydride is usually very moisture-sensitive, and can be

hydrolyzed to the corresponding carboxylic acid, resulting in the stoichiometry of two monomers being off and giving a polyimide with low molecular weight. Since an AB monomer bears two reactive groups in one molecule, it always maintains a stoichiometry balance, ensuring a high molecular weight for the polymer.

IV.1.2. Helicenes

Carbohelicenes are molecules that can be best described as exclusively carbon-containing polycyclic aromatic compounds. Their helical conformations result from the overlapping of terminal aromatic rings and as a result form a pair of conformational enantiomers. Upon resolution of these enantiomers, helicenes can show high optical rotations ($[\alpha]_D^{25}$) of the order of $1,000^\circ$ to $10,000^\circ$.⁷ The optical rotation are highly dependent on solvent and temperature. The first synthesis of an all carbon helicene molecule was performed by Newman in 1956.⁸ The synthesis of what he called hexahelicene required a total of 12 steps. The IUPAC name for this compound is phenanthro[3,4-d]phenanthrene (Figure IV.3). A simplified nomenclature proposed by Newman simply places the number of annellated aromatic ring in square brackets, followed by the word helicene. Thus, hexahelicene became [6]helicene and accordingly pentahelicene became [5]helicene which is the subject of the present research.

Figure IV.3. [6]Helicene, or hexahelicene.

Given the structure of a helicene, they have an unexpectedly low energy barrier for thermal racemization. For [5]helicene the barrier of racemization is the lowest among all helicenes, which is not surprising since it has the least interaction between the terminal rings. An interesting fact is that on the series [6]helicene to [9]helicene the energy barrier for thermal racemization is nearly constant. Additionally, all carbohelicenes fluoresce and the fluorescence band shifts to longer wavelengths along the series of helicenes with increasing [n].

Many helicenes are synthesized via a photochemical route. Cis-stilbene and trans-stilbene interconvert under ultraviolet radiation and can be photocyclized into phenanthrene in the presence of an oxidizing agent. This reaction has been used as a convenient synthetic route to higher helicenes.⁷ However, photocyclization is often carried out on unfunctionalized starting materials (i.e. molecules only containing carbon and hydrogen) in small quantities and produces unfunctionalized products in moderate yields. Therefore, photochemical routes are unsuitable to produce large quantities of helicene-based monomers.

IV.1.3. Rationale and Objectives

Based on the unique features of a helicene molecule described above, it is desirable to incorporate a helicene unit into a macromolecule to develop a novel type of polymer. First of all, the polycyclic aromatic structure of a helicene would result in a rigid, thermally stable polymer with good mechanical properties. Secondly, the non-planar, spiral shape of the monomeric units would offer a possibility for good solubility, as a result of preventing the polymer chains from packing. Additionally, the high optical rotations plus the extended array of π -systems from the helicene structure might result in an optically active polymer with a very large optical rotation which may be stable at higher temperatures.

Frimer *et al.* recently reported the synthesis of a difunctional helicene, [5]helicene-5,6,9,10-tetracarboxylic dianhydride (Figure IV.4), which involved a photochemical

cyclization.⁹ It was further demonstrated that a soluble, high molecular weight polyimide could be made by solution polymerization of this [5]helicene dianhydride and 3,3'-(hexafluoroisopropylidene)dianiline.¹⁰ The polyimides based on this novel dianhydride were found to have higher long-term thermal stability than PMR-15 thermoset resin.

Figure IV.4. [5]helicene-5,6,9,10-tetracarboxylic dianhydride.

A functionalized [5]helicene seems to be the most synthetically accessible starting point for a first attempt at incorporating a helicene unit into a polymer. Clearly, the construction of the helicene core is a crucial step in any large scale production of a [5]helicene-based monomer, which preferably should be done by a non-photochemical process. 5,6,9,10-Tetrahydro[5]helicene-7,8-dicarboxylic anhydride (IV-1, Figure IV.5) is known¹¹ and can be readily prepared in large scale in high yield from readily available starting materials using a conventional chemical processes. Given that this [5]helicene unit is functionalized with an anhydride groups on the 7 and 8 carbons, an imide can be readily formed. Making a polyimide a logical choice for a first attempt at incorporating a helicene unit into a macromolecule. If this C₂ molecule can be mononitrated, there will be an easy access to the desired AB aminoanhydride/derivative monomer containing the tetrahydro[5]helicene unit. Aromatization of the mononitrated IV-1 should convert the tetrahydro[5]helicene-based compound into the corresponding [5]helicene-based compound.

Figure IV.5. 5,6,9,10-Tetrahydro[5]helicene-7,8,-dicarboxylic anhydride (IV-1).

The objectives of the present research are to functionalize tetrahydro[5]helicene anhydride IV-1 to a suitable AB monomer and to prepare a [5]helicene-based AB monomer, and to polymerize and characterize the resulting AB polyimides.

IV.2. Synthesis of Aminoanhydride Monomers

The key starting compound, 5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic anhydride (IV-1), was readily prepared from α -tetralone and maleic anhydride in three steps (Scheme IV.1). The intermediate products in each step were used without purification. The overall yield of this three-step process was 37%. The anhydride IV-1 had a melting point of 286-287 °C, higher than that (275 or 283 °C) reported in the literature,¹¹ indicating a higher degree of purity. The whole process was easily scaled up to produce about 300 g of the final product.

Scheme IV.1. Synthesis of tetrahydro[5]helicene anhydride **IV-1**.

IV.2.1. Synthesis of Tetrahydro [5]Helicene Aminoanhydride Monomer

The crucial step in the synthesis of an AB monomer is the mononitration of the starting compound **IV-1**. Due to C_2 symmetry of **IV-1**, the two terminal benzene rings have the same reactivity toward nitration and selective mononitration would be difficult under standard nitration conditions, such as nitric acid-sulfuric acid. Indeed, nitration of **IV-1** with 70% nitric acid in concentrated sulfuric acid at $-5\text{ }^{\circ}\text{C}$ afforded the dinitro products (**IV-3**) in 94% yield. Several other conditions have been tried for mononitration. For example, nitrations using one molequiv of 70% nitric acid in 96% sulfuric acid or in acetic anhydride only led to the formation of a mixture of the mononitro compound (**IV-2**) and the dinitro compound (**IV-3**) in nearly equal amount along with unreacted **IV-1** (Scheme IV.2). TLC (30% of acetone in hexane as the developing solvent) clearly showed 3 spots corresponding to 3 compounds with different polarities. The most polar one should be the dinitro product, the least polar one corresponded to the starting material, and the mononitro compound located between the above two on TLC. The ^1H NMR and MS spectra further confirmed the formation of the dinitro compound. When nitration was carried out in acetic acid and chloroform under dilute conditions, compound **IV-1** could be

converted into the principal product **IV-2** together with a small amount of the isomer **IV-4** and the dinitro product **VI-3**. The selective mononitration with nitric acid in acetic acid and chloroform solution was usually carried out for 48 h at room temperature. Under such reaction conditions, the pure nitroanhydride **IV-2** could be obtained in 76% yield after simple workup.

Scheme IV.2. Nitration of anhydride **IV-1**.

Using both concentrated sulfuric acid and acetic anhydride with nitric acid, the reaction proceeded rapidly at $-5\text{ }^\circ\text{C}$ and still produced the dinitro product. In this case, both concentrated sulfuric acid and acetic anhydride are strong dehydrating agents and react with nitric acid rapidly to form a very powerful nitrating agent. In dilute acetic acid and chloroform solution, the power of the nitrating agent is certainly weaker. In general, the slower the reaction is, the higher the selectivity can be. Therefore, the selective nitration was successfully done under weaker nitration conditions.

The mononitrated product **IV-2** was fully characterized by spectroscopic means. The IR spectrum showed two strong absorptions at 1830 and 1763 cm^{-1} corresponding to the carbonyl groups of the anhydride group. There are also two strong bands at 1523 and 1347 cm^{-1} indicating the presence of the nitro group. The ^{13}C NMR spectrum displayed the

expected 24 signals which correlated to 24 chemically non-equivalent carbons. HRMS also confirmed the correct molecular mass. However, up to this point, it was still not clear which position the NO₂ group had substituted. There may be three possible substitution positions for this electrophilic substitution reaction. One is at the C-3 position which is *para* to the central aromatic ring, due to the para-directing nature of the phenyl group as in case A (Figure IV.6). The other is substitution at the C-1 position which is *ortho* to the central aromatic ring, due to the ortho-directing of the phenyl group as in case B (Figure IV.6). Because of steric hindrance at the C-1 position, the 1-NO₂ compound should be expected to be expected to be a minor product. The third possible substitution at the C-2 position due to the methylene group as in case C of the nitration of toluene (Figure IV.6). From the ¹H NMR spectrum, it was only clear that there was a substitution on one of the terminal aromatic rings but it was difficult to locate the substitution position. In general, when both inductive and conjugate effects exist, the latter is dominant. Therefore, in this case the nitro substitution should occur at the C-3 position rather than at the C-2 position. The ¹H NMR splitting patterns for both 2- and 3-substituted compounds should be similar. There was a singlet in the ¹H NMR spectrum, thus substitution must be either at C-2 or C-3. The substitution pattern (Figure IV.7) was further assigned with support of the COSY and NOESY experiments. From the NOESY experiment of IV-2, detection of a NOE crosspeak between the singlet aromatic H_a resonance and the aliphatic H_b resonance allows for the unambiguous assignment of the position of the nitro group at the C-3 position and not at the C-2 position. The detailed assignments are listed in Table IV.1.

Figure IV.6. Possible substitution patterns for the mononitro compound.

Table IV.1. ^1H NMR assignments of tetrahydro[5]helicene nitroanhydride IV-2.

^1H NMR	δ	J, Hz	
H_1	7.33	8.80 (1-2)	
H_2	7.80	8.72 (2-1)	2.40 (2-4)
H_4	8.23	2.36 (4-2)	
$\text{H}_5, \text{H}_{10}$	3.01	-	
H_6, H_9	4.03, 2.65	-	
H_{11}	7.39	8.00 (11-12)	
H_{12}	7.29	8.00 (12-11)	
H_{13}	6.99	8.00 (13-14)	
H_{14}	7.05	8.00 (14-13)	

Figure IV.7. ^1H NMR spectrum (400 MHz, CDCl_3) of nitroanhydride IV-2.

At first, an attempt was made to synthesize the mono-ester of **IV-5** (Figure IV.8) as the AB-type monomer. Esterification of **IV-2** with absolute ethanol was attempted. However, under the acidic condition (concentrated HCl in absolute ethanol), the esterification reaction was not complete. The starting anhydride could always be detected by TLC. When basic conditions were used with triethylamine in dichloromethane,¹² the ethyl ester could be obtained. However, the resulting product was not stable in a neutral or acidic medium and was partially converted back to the anhydride form. This indicated that the anhydride group in this compound is unusually stable, and as a consequence this anhydride may be stable even in the presence of an amine group. If so, a stable aminoanhydride (**IV-5**) could be obtained from reduction of the nitroanhydride (**IV-2**).

Figure IV.8. A mono-ester-aminodicarboxylic acid.

Indeed, when **IV-2** was reduced by hydrogenation using PtO_2 in THF at room temperature, the stable aminoanhydride **IV-5** was obtained (Scheme IV.3). Compound **IV-5** was purified by a short-column flash chromatography eluting with CH_2Cl_2 . The structure of **IV-5** was characterized by spectroscopic means. The IR spectrum confirmed the presence of the carbonyl bands (1826 and 1759 cm^{-1}) for the anhydride, and the primary amino group (3368 and 3488 cm^{-1}). HRMS gave the expected mass. The ^{13}C NMR spectrum showed the expected 24 peaks. The ^1H NMR spectrum is shown in Figure IV.9, and the assignments supported by COSY experiment are listed in Table IV.2. Besides all the spectroscopic evidence, the structure of the aminoanhydride monomer was verified by single crystal X-ray diffraction analysis (Figure IV.10). The crystal structure

shows that the two terminal aromatic rings are non-planar with an inter-planar angle of 50.9°. The amino and anhydride groups are connected by a conjugated biphenyl moiety to form a “push-and-pull” system.

Scheme IV.3. Reduction of the nitroanhydride IV-2 to the aminoanhydride IV-5.

Table IV.2. ¹H NMR assignments of the aminoanhydride IV-5.

¹ H NMR	δ	J, Hz	
H ₁	7.00	8.28 (1-2)	
H ₂	6.28	8.40 (2-1)	2.40 (2-4)
H ₄	6.61	2.40 (4-2)	
H ₅ , H ₁₀	2.83	-	
H ₆ , H ₉	3.91, 2.56	-	
H ₁₁	7.31	8.00 (11-12)	
H ₁₂	7.21	8.00 (12-11)	
H ₁₃	6.99	8.00 (13-14)	
H ₁₄	7.33	8.00 (14-13)	

Figure IV.9. ^1H NMR of the tetrahydro[5]helicene-aminoanhydride IV-5.

Figure IV.10. Molecular structure of the aminoanhydride IV-5 in its crystal form.

Unlike 3- and 4-aminophthalic anhydrides which do not show any melting points by gradual heating (the melting point measured by drop melting), the aminoanhydride **IV-5** displays a sharp melting point, 181.8 °C by DSC (heating rate at 10 °C/min) or 181-183 °C by gradual heating on a melting point apparatus. At a temperature higher than its melting point, condensation reaction took place rapidly to yield water and oligoimides. DSC curves for the aminoanhydride are shown in Figure IV.11. In the first run, a clear melting endotherm was observed. In the second and third runs, the melting point disappeared, and a weak transition at about 300 °C might indicate the loss of water due to further imidization. This aminoanhydride is stable in refluxing chloroform and TCE but becomes reactive in polar solvents such as DMSO, DMAc and NMP at elevated temperatures. This clearly indicates that **IV-5** meets the two criteria for an ideal AB aminoanhydride monomer: stable and unreactive at ambient temperatures so that purification is possible and yet, sufficiently reactive at elevated temperatures to make polymerization possible.

Figure IV.11. DSC curves of the aminoanhydride IV-5.

IV.2.2. Synthesis of [5]Helicene Aminoanhydride Monomer

The [5]helicene-based aminoanhydride monomer **IV-7** was synthesized by aromatization of the tetrahydro[5]helicene-nitroanhydride **IV-2** by bromination and then reduction of the [5]helicene-nitroanhydride **IV-6** (Scheme IV.4). The resulting [5]helicene aminoanhydride (**IV-7**) can be purified by sublimation under high vacuum (5 mmHg) at ca 200 °C without any self condensation. It showed similar behavior to the tetrahydro[5]helicene aminoanhydride **IV-5** upon heating by DSC. The melting temperature (331.7 °C) could be clearly seen in the first DSC run, and disappeared in the second and the third runs. This aminoanhydride is also stable in chlorinated hydrocarbon solvents such as CHCl_3 at 80 °C and TCE at 150 °C. It becomes reactive in polar solvents like DMSO, DMAc and NMP (e.g., even at room temperature in DMSO) as **IV-5**.

Scheme IV.4. Synthesis of [5]helicene aminoanhydride monomer **IV-7**.

The structure of **IV-7** was verified by IR, NMR and HRMS. The primary amine appeared at 3366 and 3490 cm^{-1} , and the carbonyl of the anhydride showed at 1830 and 1751 cm^{-1} in the IR spectrum. The bands at 1612 cm^{-1} indicated the presence of aromatic C-C double bonds. There was no C-H bands close to the 3000 cm^{-1} line, which appeared in the IR spectrum of the tetrahydro[5]helicene aminoanhydride **IV-5**, indicating the fully aromatic system for the [5]helicene aminoanhydride monomer. Unfortunately, it was not soluble enough in chloroform for NMR measurement. Although soluble in DMSO, it tends to self condense slowly (over 24 h) in this polar solvent. Nevertheless, the ^1H NMR spectrum of **IV-7** in DMSO-d_6 showed no aliphatic protons and the ^{13}C NMR spectrum

displayed all 24 chemically non-equivalent carbons. HRMS further confirmed the molecular mass.

IV.3. Synthesis and Characterization of Tetrahydro[5]helicene Polyimide

As mentioned in Chapter I, in order to use the one-step polymerization to produce a high molecular weight polyimide, both the monomer and the resulting polymer must be soluble in the solvent of polymerization. The twisted *o*-terphenyl moiety and aliphatic ethylene units were able to impart good solubility to tetrahydro[5]helicene monomer **IV-5** and the resulting polyimide **IV-8**, because one-step polymerization was carried out in 6% *m*-cresol solution in the presence of a small amount of isoquinoline at 200 °C (Scheme IV.5). The detailed procedure was same as the one described in Chapter II. High molecular weight polyimide **IV-8** could be obtained in about 18 h. It had a weight-average molecular weight of 188,000 by GPC relative to polystyrene and a polydispersity index of 2.23. Intrinsic viscosity was 0.84 dL/g in TCE at 30 °C, indicating the high molecular weight of **IV-8**.

Conversion of the amino into the imido group should significantly diminish the electron-donating power of the amino group, as evidenced by a similarity of polyimide IV-8 and anhydride IV-1 in its absorption spectra (spectra a and b). A similar electronic effect was also observed in the ^1H NMR spectra, there were only a set of multiple peaks for the aromatic protons in the spectrum of polyimide IV-8 and the peak positions were close to those for anhydride IV-1.

Figure IV.13. UV-vis spectra (5.0×10^{-5} M, chloroform) of (a) anhydride IV-1, (b) polyimide IV-8 and (c) monomer IV-5.

Polyimide **IV-8** was readily soluble in TCE and showed limited solubility in chloroform and NMP at ambient temperatures. It was more soluble in chlorinated hydrocarbon solvents like CHCl_3 and TCE than polar solvents such as DMAc, DMF and DMSO. This might be due to the high carbon-hydrogen content of tetrahydro[5]helicene unit and low imide component. The polyimide **IV-8** appears to be less polar than most polyimides reported based on its limited solubility in polar organic solvents.

Polyimide **IV-8** was further characterized by DSC, TGA and DMA. The glass transition temperature (T_g) could not be detected by DSC or DMA up to 450 °C, indicative of the high rigidity of the polymer backbone. In general, with increasing chain stiffness the detection of glass transitions by DSC becomes more difficult. Despite the presence of aliphatic moieties, polyimide **IV-8** displayed good thermal stability. The onset temperature for 5% weight loss in nitrogen was at 499 °C, as assessed by TGA. In air, the onset temperature was 455 °C, still comparable to most of the polyimides reported.

A clear, flexible and tough film could be cast from the TCE solution of **IV-8**. Young's modulus of the non-oriented, amorphous film was measured to be 2.91 GPa at 25 °C and 2.36 GPa at 200 °C using DMA in a tensile stress-strain mode.

IV.4. Synthesis and Characterization of [5]Helicene Polyimide

IV.4.1. Synthesis of [5]Helicene Polyimide by Direct Polycondensation

Solution polymerization of the [5]helicene-based monomer **IV-6** was attempted in *m*-cresol (2% concentration) at 200 °C, but only a low molecular weight insoluble oligomer was formed (Scheme IV.6). The premature oligoimide **IV-9** precipitated from the reaction solution, and the isolated product was not soluble in any solvent including concentrated sulfuric acid. The insolubility is probably due to the high rigidity of the fully aromatic polymer backbone. The IR spectrum of oligomer **IV-9** showed the imido carbonyl bands at 1767 and 1716 cm^{-1} .

Scheme IV.6. Attempt one-step polymerization of monomer IV-6 to [5]helicene polyimide IV-9.

IV.4.2. [5]Helicene Polyimide Synthesized by Polymer Transformation

Due to the poor solubility, rigid polymers often can not be obtained in high molecular weight by one-step solution polymerization. The precipitation of oligomers or ill-defined materials is often the case for this type of polymer. In order to overcome this problem, a precursor strategy can be used which involves the synthesis of a soluble polymer precursor followed by polymer transformation to yield the final rigid polymer. The polymer transformation can be done by means of photochemical process,¹³ thermal curing,¹⁴ or chemical processes.¹⁵ Among these methods, a chemical transformation offers the most versatile process, because many reactive groups within a polymer can be converted chemically into a cyclic functionality while only a few functional groups are reactive toward heat and light. For instance, poly(p-phenylene) is a very rigid polymer which can not be synthesized by direct polymerization due to its poor solubility. The precursor strategy has been successfully used to produce high molecular weight poly(p-phenylene). The soluble, non-aromatic cyclic polymer (Scheme IV.7) was synthesized first in high molecular weight as a polymer precursor. The insoluble, rigid poly(p-phenylene) was then obtained by thermolysis of the soluble polymer precursor (Scheme IV.7).¹⁶

Scheme IV.7. High molecular weight poly(*p*-phenylene) synthesized by polymer transformation.

In our case, although the [5]helicene AB polyimide can not be made by one-step solution polycondensation directly from the aminoanhydride IV-6, high molecular weight polymer IV-9 could be obtained from polyimide IV-8 and used as a precursor polymer.

As a model reaction, the tetrahydro[5]helicene anhydride IV-1 was converted quantitatively into [5]helicene anhydride IV-10 upon treatment with elemental bromine at elevated temperatures (Scheme IV.8). This aromatization reaction was found to be best carried out by adding bromine to the substrate in hot TCE or *o*-dichlorobenzene at temperatures of 150–180 °C. If the reaction is run at lower temperatures or from room temperature to high temperature, the desired product is obtained in low yield with brominated by-products. A plausible explanation for this aromatization reaction, is that under high temperature conditions, bromine is homolytically cleaved to generate a bromine radical which abstracts a hydrogen radical at the benzylic position. Another $\text{Br}^\bullet$ is added and then subsequently eliminated to produce HBr , which occurs spontaneously at high temperature to form a carbon-carbon double bond. The radical mechanism was further confirmed by using *N*-bromosuccinimide (NBS) as the bromine radical source. The

aromatization reaction was completed at 140 °C in 1 h. The fully aromatized product was identical spectroscopically to the one made by aromatization with elemental bromine.

Scheme IV.8. Model reaction for aromatization with bromine.

Based on this model reaction, polyimide IV-8 was subjected to aromatization with bromine to yield polyimide IV-9 (Scheme IV.9). Thus, upon addition of bromine into a refluxing TCE solution of polyimide IV-8, the yellow polyimide IV-9 precipitated out immediately. This polymer transformation was also performed on the solid film. The free-standing thin film of IV-8 was treated with bromine vapor at high temperature (ca. 260 °C) and converted into polyimide IV-9 without thermal or chemical degradation. Lassaigne's test¹⁷ on polyimide IV-9 gave a negative result, indicating the absence of any residual bromine. Completion of the chemical transformation or aromatization was unambiguously confirmed by FTIR. Figure IV-14 shows the IR spectra of the precursor polyimide IV-8, oligomer IV-9 made by solution polymerization of IV-6 and the film of IV-9 derived from the film of IV-8. The aliphatic C-H bands are clearly seen close to the right side of the 3000 cm⁻¹ line for polyimide IV-8 (spectrum a) and are completely vanished for polyimide IV-9 (spectrum c). The spectra of the powdered oligomer IV-9 and the polymer film IV-9 are almost superimposable.

Scheme IV.9. Polyimide transformation from IV-8 to IV-9.

In fact, the bromination reaction can be accomplished at a lower temperature with NBS than with elemental bromine. Although the reactions have not been utilized for the conversion of the tetrahydro[5]helicene polyimide to the corresponding [5]helicene polyimide, one could foresee that the degrees of bromination on the tetrahydro[5]helicene unit could be controlled by the amount of NBS used. For example, a random copolyimide might contain the structures of tetrahydro[5]helicene, [5]helicene and dihydro[5]helicene (Scheme IV.10) by partial aromatization using one mole of NBS to the starting tetrahydro[5]helicene polyimide. The copolyimides synthesized as such might display different degrees in solubility depending on the degree of aromatization.

Scheme IV.10. The possible structure of random copolyimide by bromination of NBS.

Figure IV.14. IR spectra of (a) polyimide IV-8, (b) oligomer IV-9 (derived from IV-6) and (c) polyimide IV-9 (derived from IV-8).

Due to the presence of the helicene moiety, the polyimide film of **IV-9** had a higher thermal stability than that of the precursor polyimide **IV-8**, with the onset temperature for 5% weight loss at 537 °C in nitrogen and 485 °C in air. The tensile modulus (6.34 GPa at 25 °C) of the polyimide film **IV-9** was higher than that (2.91 GPa) of polyimide **IV-8** and remained high (5.48 GPa) even at 200 °C. The film of **IV-9** has a much higher tensile modulus than most commercially available unoriented and even some oriented polyimide films. For example, the biaxially oriented Kapton® has a tensile modulus of 2.96 GPa.¹⁸ The high rigidity of [5]helicene-based polyimide is certainly responsible for its high tensile modulus. No T_g for **IV-9** could be detected by DSC or TMA up to 500 °C.

IV.5. Conclusion

The first AB-type aminoanhydride monomer (e.g., **IV-5**) can be obtained in high purity and polymerized to the corresponding polyimide of high molecular weight. Therefore, it is highly possible that other interesting aromatic aminoanhydrides could be designed, synthesized and polymerized. It has also been demonstrated that a [5]helicene moiety could be incorporated into the polyimide main chain by chemical transformation of a precursor polymer in solution or in the solid state.

IV.6. Experimental

Materials.

α-Tetralone, maleic anhydride, bromine and N-bromosuccinimide (NBS) were purchased from Aldrich Chemical Co. and used as received. 1,1,2,2-Tetrachloroethane (TCE), dimethylsulfoxide (DMSO) N,N-dimethylacetamide (DMAc), N-methyl-2-pyrrolidinone (NMP), N,N-dimethylformamide (DMF) and other common organic solvents (Aldrich) were reagent grade unless otherwise stated and used as received.

Characterization.

The equipment and methods for characterization are same as those described in Chapter II.

X-ray structure determination of IV-5.

Crystal structure determination was performed at the department of chemistry of the University of Ottawa, Ottawa, Canada. The single crystal of IV-5 was grown from chloroform solution at ambient temperature and cut with dimensions of 0.2 mm x 0.2 mm x 0.2 mm. All the measurements were made on a Nonius diffractometer with Cu K α radiation. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement using the setting angles of 25 reflections in the range $100 < 2\theta < 130$ corresponded to a monoclinic cell with dimensions: $a = 8.4531(8) \text{ \AA}$, $b = 23.854(3) \text{ \AA}$, $c = 11.0902(11) \text{ \AA}$, $\beta = 103.275(8)^\circ$. For $Z = 4$ and $FW = 496.94$, the calculated density is 1.517 g/cm^3 . Based on the systematic absences, the space group was determined to be $P 2_1/c$. The data were collected at -110°C using the omega- 2θ scan technique to a maximum 2θ value of 128.4 . The residuals are as follows: for significant reflections, $R_f = 0.063$, $R_w = 0.078$; for all reflections, $R_f = 0.076$, $R_w = 0.080$. A total of 5549 reflections was collected. The unique set contains only 3259 reflections. The standards were measured after every 150 reflections. No crystal decay was noticed. The data were collected for Lorentz and polarization effects. No absorption correction was made. The structure was solved by direct methods. There is two molecules per asymmetric unit. All the phenyl groups were refined as rigid group to increase the ratio reflections/parameters. All the atoms were refined anisotropically except the hydrogen. The hydrogen atoms were calculated assuming a distance C-H of $1.007 \text{ \AA}$. Calculations were performed using the NRCVAX crystallographic software package.

Monomer Synthesis

5,6,9,10-Tetrahydro[5]helicene-7,8-dicarboxylic anhydride (IV-1).

The reported procedure¹¹ was modified for large-scale preparation as follows: (a) In a 10 L reaction vessel α -tetralone (1200 g, 8.20 mol) was dissolved in 3.5 L of toluene and 2.0 L absolute ethanol. To this solution aluminum foil (227 g, 8.40 mol) and HgCl_2 (7.00 g, 25.0 mmol) were added and the solution was set to a vigorous stir with gentle heating. The reaction was sufficiently exothermic to the solvent to reflux. After 4 h reaction, an aqueous HCl solution (800 mL conc. HCl diluted to 4 L) was added in one portion and the resulting heterogeneous mixture was allowed to stir overnight. The organic phase was decanted, dried over MgSO_4 and removed to yield the pinacol product as a slightly yellow solid. The remaining aqueous phase was extracted with diethyl ether (3 x 3 L). The ethereal extract was dried and removed to yield more product. The yield was 867 g (71%). This product (498 g, 1.70 mol) was mixed in a solution of 600 mL of acetic anhydride and 400 mL of acetic acid and refluxed overnight. The reaction was allowed to cool to room temperature and the precipitate was filtered to give the corresponding diene (329 g, 74%). (b) The diene (329 g, 1.30 mol) and maleic anhydride (950 g, 9.70 mol) were placed in an Erlenmeyer flask and heated at 155 °C for 3 h. While still hot and homogeneous, the reaction mixture was dumped into 2.0 L of hot water with vigorous stirring. The resulting slurry was stirred for 2 h. The solid was filtered and divided into two portions which were then stirred in water (2 L each) overnight. The solid was filtered and washed with 450 mL of glacial acetic acid. The solid was once again filtered and dried. The corresponding Diels-Alder adducts of endo and exo isomers was obtained (387 g, 85%). (c) The Diels-Alder

products (385 g, 1.10 mol) were dissolved in chloroform (2.1 L) and stirred at room temperature in a 4 L, 3-necked, round-bottomed flask fitted with a gas outlet routed to an aqueous KOH solution. To this chloroform solution, Br₂ (440 g, 2.80 mol) in acetic acid (200 mL) was added dropwise over 1.5 h. The reaction mixture was allowed to stir at room temperature overnight. The precipitate was filtered, washed with methanol (2 x 1.0 L) and dried (60-80 °C, 5 mmHg) to give anhydride **IV-1**: 317 g (82% or 37% yield based on α -tetralone); mp 286-287 °C (lit^{11a} 282 °C, lit^{11b} 275 °C).

3-Nitro-5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic anhydride (IV-2).

Anhydride **IV-1** (30.0 g, 85.2 mmol) was dissolved in 1.0 L of chloroform, to which was added 300 mL of acetic acid. The nitrating agent (300 g of 70% nitric acid and 250 g of concentrated sulfuric acid in 500 mL of acetic acid) was added dropwise into the above solution at room temperature (22 °C). The reaction continued for 4 h until TLC showed no more starting material. The solution was then poured onto 500 g of crushed ice with vigorous stirring. The yellow precipitates were collected. After washing twice with methanol and drying in a vacuum oven (60 °C, 5 mmHg), pure 3-nitroanhydride **IV-2** (26.0 g, 76%) was obtained. Evaporation of excess methanol in filtrate afforded 6.6 g (20%) of a mixture of isomeric 1- and 3-nitro products in about a 1:1 ratio. The 3-nitro product **IV-2** could be recrystallized from a mixture of acetonitrile and dichloromethane as a yellow crystalline solids. mp 267.3 °C (DSC); IR (KBr, C=O) 1763, 1830 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.23 (1 H, d, J = 2.36 Hz), 7.80 (1 H, q, J = 2.36 Hz, J = 4.36 Hz), 7.34 (3 H, m), 7.01 (2 H, m), 4.02 (2 H, t, J = 19.3 Hz), 3.07 (4 H, m), 2.64

(2 H, m); ^{13}C NMR (50 MHz, CDCl_3) δ 162.78, 162.74, 147.31, 142.21, 140.95, 140.60, 140.42, 139.34, 138.37, 132.07, 130.92, 130.41, 129.90, 128.46, 126.91, 126.52, 125.65, 123.29, 123.13, 121.13, 28.26, 28.10, 24.18, 24.11; MS (EI, m/e, relative intensity %) 397 (M^+ , 100).

3-Amino-5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic anhydride (IV-5).

The 3-nitroanhydride IV-2 (1.00 g) was dissolved in 50 mL of THF containing 3 drops of water and 15 mg of PtO_2 catalyst. Under 40 psi of hydrogen, the nitro compound was reduced to the corresponding amine at room temperature in 3 h. The catalyst was filtered and the solution was dried over MgSO_4 . Removal of THF under reduced pressure (20 mmHg) and drying at room temperature afforded the reddish solid (0.83 g, 90%). The product IV-5 was further purified by flash chromatography on a short column eluting with dichloromethane: 0.66 g (72%); mp 181-183 $^\circ\text{C}$, 181.8 $^\circ\text{C}$ (DSC); IR (KBr, $\text{C}=\text{O}$) 1826, 1759 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.33 (2 H, m), 7.21 (1 H, m), 6.99 (2 H, m), 6.61 (1 H, d, $J = 2.4$ Hz), 6.28 (2 H, q, $J = 2.4$ Hz, $J = 6.02$ Hz), 3.91 (4 H m), 2.88 (4 H, m) 2.56 (2 H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 163.56, 163.42, 147.42, 141.59, 140.89, 140.57, 139.55, 139.27, 138.85, 133.50, 131.72, 131.27, 129.55, 128.89, 128.63, 128.41, 128.27, 127.85, 126.25, 126.00, 125.30, 125.14, 123.81, 123.43, 121.03, 113.40, 113.15, 112.79, 28.45, 28.28, 24.55, 24.25; MS (EI, m/e, relative intensity %) 367 (M^+ , 100); HRMS calcd for $\text{C}_{24}\text{H}_{17}\text{NO}_3$ 367.1208, found 367.1196.

3-Nitro-[5]helicene-7,8-dicarboxylic anhydride (IV-6).

Anhydride **IV-2** (5.00 g, 12.59 mmol) was dissolved in 35 mL of 1,2-dichlorobenzene and heated to reflux at 180 °C. Br₂ (4.40 g, 27.84 mmol) was added, and the colour of bromine disappeared immediately. The reaction continued for 2 h. The solution was then cooled to room temperature and poured into 100 mL of methanol. The resulting yellow product **IV-6** was collected and dried in a vacuum oven (60-80 °C, 5 mmHg): 4.72 g (96%); mp 300.7 °C (DSC); IR (KBr, C=O) 1838, 1763 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 9.10 (1 H, d, J = 8.76 Hz), 8.97 (1 H, d, J = 5.40 Hz), 8.95 (1 H, d,), 8.55 (1 H, d, J = 9.32 Hz), 8.28 (3 H, m), 8.08 (2 H, m), 7.73 (1 H, m), 7.40 (1 H, m); ¹³C NMR (50 MHz, CDCl₃) δ 162.97, 146.68, 134.10, 133.69, 133.05, 133.01, 131.81, 131.76, 131.21, 131.00, 129.91, 129.46, 129.32, 128.73, 128.33, 127.73, 126.72, 126.40, 126.36, 124.27, 123.32, 120.93, 119.03; MS (EI, m/e, relative intensity %) 393 (M⁺, 100).

3-Amino-[5]helicene-7,8-dicarboxylic anhydride (IV-7).

Nitroanhydride **IV-6** (1.00 g) was dissolved in 75 mL of THF containing 3 drops of water and 15 mg of PtO₂ catalyst. Under 40 psi of hydrogen, the nitro compound was

reduced to the corresponding amine at room temperature in 2 h. After filtration of the catalyst, the filtrate was dried over MgSO_4 and concentrated under reduced pressure. Hexane (20 mL) was then added into the residue to precipitate the product **IV-7** which was usually pure enough for polymerization. It could be further purified by sublimation in vacuo at ca 200 °C to give a purple crystalline solid: 0.70 g (81%); mp 331.7 °C (DSC); IR (KBr, C=O) 1833, 1751 cm^{-1} ; ^1H NMR (200 MHz, DMSO-d_6) δ 8.68 (1 H, d, J = 8.80 Hz), 8.55 (1 H, d, 8.84 Hz), 8.38 (1 H, d, 8.44 Hz), 8.28 (1 H, d, J = 8.80 Hz), 8.13 (1 H, d, J = 7.24 Hz), 7.99 (1 H, d, J = 8.82 Hz), 7.91 (1 H, d, J = 9.16 Hz), 7.68 (1 H, t, J = 6.96 Hz), 7.40 (1 H, t, 7.00 Hz), 7.03 (1 H, d, J = 2.36 Hz), 6.72 (1 H, q, J = 9.16 Hz, J = 2.36 Hz), 6.12 (2 H, s); ^{13}C NMR (50 MHz, CDCl_3) δ 163.84, 163.64, 149.85, 135.92, 132.96, 132.81, 130.55, 130.40, 130.22, 130.03, 129.92, 128.31, 128.10, 127.84, 126.99, 125.85, 125.63, 123.19, 123.02, 121.04, 120.21, 116.21, 107.11, 106.69; MS (EI, m/e , relative intensity %) 363 (M^+ , 45); HRMS calcd for $\text{C}_{24}\text{H}_{13}\text{NO}_3$ 363.0895, found 363.0888.

Model Chemical Transformation

[5]Helicene-7,8-dicarboxylic anhydride (**IV-10**).

To a boiling solution of anhydride **IV-1** (1.00 g, 2.84 mmol) in TCE (10 mL), was added Br_2 (1.13 g, 7.10 mmol) dropwise over 10 min. After 1 h the reaction solution was cooled to room temperature and poured into 50 mL of hexane. The resulting yellow precipitate was collected by filtration, washed twice with hot hexane, and dried in a vacuum oven (5 mmHg) at 130 °C. The pure anhydride **IV-10** was obtained as a yellow solid and

could be further recrystallized from DMAc: 0.96 g (97%); mp 276-277 °C, 275.7 °C (DSC) (lit^{11a} >360 °C); IR (KBr, C=O) 1839, 1756 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.91 (1 H, d, J = 8.76 Hz), 8.39 (1 H, d, J = 8.56 Hz), 8.15 (1 H, d, J = 8.76 Hz), 8.02 (1 H, d, J = 8.04 Hz), 7.64 (1 H, t d, J₁ = 1.00 Hz, J₂ = 8.04 Hz), 7.31 (1 H, t d, J₁ = 1.00 Hz, J₂ = 8.56 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 163.52, 133.77, 132.90, 131.00, 130.43, 129.54, 128.80, 128.33, 126.53, 126.38, 125.68, 120.96; HRMS calcd for C₂₄H₁₂O₃ 348.0786, found 348.0798.

Bromination with NBS

A solution of anhydride **IV-1** (0.50g, 1.42 mmol) and NBS (0.53 g, 2.88 mmol) in TCE (10 mL) was heated to 140-150 °C. The solution became brown 10 min after the reaction started. HBr evolution could be detected by a wet pH paper. The reaction was followed by TLC. After 1 h, the reaction solution was cooled to room temperature and poured into 20 mL of methanol. The yellow precipitate was washed twice with methanol, and dried in an oven at 130 °C. The anhydride **IV-10** was obtained as a yellow solid and could be further recrystallized from DMAc: 0.44 (90%); mp 275-276 °C. The spectroscopic data were identical to those obtained for **IV-10** made by using bromine.

Polymer Synthesis

Polyimide **IV-8**.

Monomer **IV-5** (0.50 g) was dissolved in 8.5 mL of *m*-cresol in a 3-neck, round-bottomed flask fitted with a nitrogen inlet, a nitrogen outlet and a magnetic stirrer. The solution was stirred at 200 °C under a flow of nitrogen overnight. The resulting viscous solution was cooled to 100 °C and then poured into 200 mL of methanol. The yellow polymer was collected by filtration. Washing with hot acetone several times and drying in a vacuum oven (5 mmHg) at 150 °C overnight gave polyimide **IV-8**: 0.43 g (92%); IR (KBr, C=O) 1764, 1712 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.23 (7 H, m), 4.12 (2 H, s), 2.99 (4 H, d), 2.62 (2 H, s); Mw = 188,000 (GPC), DP = 2.23; [η] = 0.84 dL/g (TCE, 30 °C). T_d (5% weight loss in nitrogen) = 499 °C; E' = 2.91 GPa (25 °C), 2.36 GPa (200 °C).

Oligoimide **IV-9**.

The [5]helicene aminoanhydride **IV-7** (0.2 g) was heated in a *m*-cresol (10 mL) solution to 200 °C. The solid was rapidly precipitated out after the temperature reached 180 °C. With increasing temperature to 220 °C, the solid was still not soluble. The reaction was carried on for 2 days. The suspension was poured into acetone (50 mL). By filtration, the reddish product was collected. Washing with acetone several times and drying in a high vacuum oven (5 mmHg) at 120 °C yielded 0.16 g of the product (76%), which was not soluble in any organic solvents.

Polyimide IV-9.

(a) In solution: The powdered polyimide IV-8 (0.10 g) was dissolved in 7.5 mL of TCE and heated to reflux. Br₂ (3 drops, ca. 0.4 g) was added to the solution while refluxing. A yellow precipitate formed spontaneously. The reaction continued for 1 h at the same temperature. The solution was then cooled to room temperature. The resulting polyimide IV-9 was collected by filtration, washed with acetone several times, and dried at reduced pressure (5 mmHg) at 150 °C for 2 days. The powdered polymer IV-9 (0.95 g, 96%) was placed in a round-bottomed flask and was heated at 350 °C for 40 min under nitrogen atmosphere. IR (KBr, C=O) 1767, 1716 cm⁻¹; T_d (5% weight loss in nitrogen) = 495 °C. The test for bromine was negative.

(b) As a film: The polyimide film cast from the TCE solution of IV-8 was placed in a glass container fitted with a vacuum outlet and a gas inlet. The container was evacuated by a water aspirator (20-30 mmHg) and was heated in a sand bath at 270 °C for 3 h. A small amount of bromine vapour was then introduced into the container through the gas inlet. After Br₂ was kept inside for 20 min at 270 °C, the vacuum was applied with a water aspirator (20-30 mmHg) for 2 h to remove both bromine and HBr. The film IV-9 was then allowed to cool to room temperature and characterized. IR (KBr, C=O) 1767 and 1716 cm⁻¹; T_d (5% weight loss in nitrogen) = 537 °C; E' = 6.34 GPa (25 °C), 5.48 GPa (200 °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 **IV-9** (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, 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 the 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 nitric acid. The silver nitrate solution (1 mL) was added into the filtrate. The resulting clear solution indicated no bromine present within the polymer sample.

References

1. (a) Borgert, M. T.; Renshaw, R. R. *J. Am. Chem. Soc.* **1908**, *30*, 1135. (b) D'Alello, G. F. *U.S. Pat.* 4,064,113; 1977. *Chem. Abstr.* 88:121903x.
2. It is available from Aldrich Chemical Co. and can be recrystallized from nitrobenzene as moisture-sensitive orange needles with mp > 350 °C. *Beil.* 18(2), 469.
3. Coudance, J.; Vert, M., *Eur. Polym. J.* **1987**, *23*(7), 501.
4. (a) Yamazaki, N.; Higashi, F. *Polym. Lett.* **1974**, *12*, 185. (b) Yamazaki, N.; Higashi, F. *Polym. Preprints. (Am. Chem. Soc. Div. Polym. Chem.)* **1977**, *17* (1), 157. (c) Higashi, F.; Akiyama, N.; Ogata, S. *J. Polym. Sci., Part A: Polym. Chem.* **1983**, *21*, 913.
5. Darmory, F. P. *Adh. Age.* **1974**, *17*, 22.
6. Feld, W. A.; Genez, B. J.; Friar, L. L.; Serico, L. *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **1978**, *19*(1), 552.
7. (a) Laarhoven, W. H.; Prinsen, W. J. C. *Topics in Current Chemistry: Stereochemistry.* **1984**, *125*, 63. (b) Meuer, K. P.; Vogtle, F. *Topics in Current Chemistry: Organic Chemistry.* **1985**, *127*, 32.
8. Newman, M. S. *J. Am. Chem. Soc.* **1956**, *78*, 4756.

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9. Frimer, A. A.; Kinder, J. D.; Youngs, W. J.; Meador, M. A. B. *J. Org. Chem.* **1995**, *60*, 1658.
10. Frimer, A. A.; Cavano, P. J.; Alston, W. B. *High Perform. Polym.* **1995**, *7*, 93.
11. (a) Weidlich, H. A. *Ber.* **1938**, *71*, 1203. (b) Bergmann, F.; Eschinazi, H. E.; Neeman, M., *J. Org. Chem.* **1943**, *8*, 179.
12. Hassner, A.; Alexanian, V. *Tetrahedron Lett.* **1978**, *46*, 4475.
13. Mullen, K.; Bihm, A.; Fiesser, G.; Garay, R. O.; Mauermann, H.; Stein, S. *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **1993**, *43 (1)*, 195.
14. Lindley, P. M.; Reinhardt, B. A. *J. Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 1061.
15. (a) Wang, Z. Y.; Zhang, C. *Macromolecules*, **1992**, *25*, 5851. (b) Zhang, C.; Wang, Z. Y. *Macromolecules*, **1993**, *26*, 3330. (c) Wang, Z. Y.; Zhang, C.; Arnoux, F. *Macromolecules*, **1994**, *27*, 4415.
16. Gin, D. L.; Conticello, V. P.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 3167.
17. Vogel, A. I. "Vogel's Textbook of Practical Organic Chemistry", 5th Ed., Longman Scientific & Technical and John Wiley & Sons: New York, **1989**, pp 1205 - 1208.
18. Hergenrother, P. M. *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1262.