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SYNTHESIS AND PROPERTIES OF NOVEL POLYIMIDES

By

Hai Bin Zheng, M.Eng.

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

**Department of Chemistry
Carleton University
Ottawa, Ontario, Canada
07/2001**

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The undersigned hereby recommend to
the Faculty of Graduate Studies and Research
acceptance of the thesis,

Synthesis and Properties of Novel Polyimides

Submitted by
Hai Bin Zheng, B.Sc., M.Sc.

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

Chair, Department of Chemistry

Thesis Supervisor

External Examiner

Carleton University
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ABSTRACT

This thesis focuses on the design and synthesis of novel dihalide and dianhydride monomers as one of the common approaches to attain new polyimides with desired properties. The designs of new monomers are rationalized based on the known structure-property relationship of polyimides.

The naphthalimide moiety was incorporated into dihalide monomers which were polymerized with bisphenols to obtain a series of new poly(ether naphthalimide)s. The poly(ether naphthalimide)s displayed glass transition temperatures of 283-342 °C and excellent solubility in common organic solvents. The onset temperatures for 5% weight loss in nitrogen for the poly(ether naphthalimide)s were over 448 °C. In addition to the desired physical properties, the poly(ether naphthalimide)s showed electroactive and electrochromic properties. The electroactive sites within poly(ether naphthalimide)s were identified to be the ketone and imide groups. The stepwise coloration process of poly(ether naphthalimide) films from colorless to red and dark blue can be achieved and controlled electrically.

The synthesis of a new unsymmetric dianhydride was also described in this thesis. Both naphthalic and phthalic anhydrides presented in the unsymmetric dianhydride showed different reactivity towards aromatic amine and the resulting polyimides displayed the improved solubility and thermal stability. The glass transition temperatures of the polyimides were in the range of 285-370 °C, and the onset temperatures for 5% weight loss in nitrogen were over 476 °C. The polyimides derived from the unsymmetric dianhydride were also electrochromic due to the presence of electroactive sites of ketone

and imide groups. Moreover, due to the different reactivity of naphthalic and phthalic anhydride groups, this novel unsymmetric dianhydride was successfully used as an end capping agent to prepare reactive oligoimides, well suited for the synthesis of segmented block copolyimides.

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SYMBOLS AND ABBREVIATIONS

BAPP	2,2'-Bis(4-[4-aminophenoxy]phenyl)propane
BNTDA	1-Benzoylnaphthalene-3',4,4',5-tetracarboxylic dianhydride
BTDA	3,3',4,4'-Benzophenonetetracarboxylic dianhydride
BPA	Bisphenol A or 4,4'-(Isopropylidene)diphenol
BPDA	3,3',4,4'-Biphenyltetratetracarboxylic dianhydride
COSY	Correlated spectroscopy
CV	Cyclic voltammogram
δ	Chemical shift (ppm)
DSC	Differential scanning calorimetry
DMAc	N,N-Dimethylacetamide
DMF	N,N-Dimethylformamide
E'	Young's modulus
E _{pc1}	Potential of first cathodic peak
E _{pa1}	Potential of first anodic peak
6FDA	4,4'-(Hexafluoroisopropylidene)diphthalic anhydride
6FBPA	4,4'-(Hexafluoroisopropylidene)diphenol
GPC	Gel permeation chromatography
HETCOR	Heteronuclear shift correlation
HPLC	High performance liquid chromatography
HRMS	High resolution mass spectroscopy
IR	Infrared

ITO	Indium tin oxide
J	Coupling constant
MDA	4,4'-Methylenediamine
Mn	Number average molecular weight
Mw	Weight average molecular weight
Mp	Melting point
MS	Mass spectrometry
NMP	1-Methyl-2-pyrrolidinone
NMR	Nuclear magnetic resonance
NTDA	1,4,5,8-Naphthalenetetrocarboxylic dianhydride
ODA	4,4'-Oxydianiline
ODPA	Oxydiphthalic anhydride
PMDA	Pyromellitic dianhydride
PTDA	3,4,9,10-Perylenetetrocarboxylic dianhydride
PC	Propylene carbonate
Tan δ	Loss tangent
TCE	1,1,2,2-Tetrachloroethane
TBAPC	Tetra-n-butylammonium perchlorate
Td	Decomposition temperature
Tg	Glass transition temperature
TG	Thermogravimetry
THF	Tetrahydrofuran
Tm	Melting temperature

TLC	Thin layer chromatography
TMA	Thermomechanical analysis
UV/Vis/NIR	Ultraviolet/visible/near infrared

Chapter I

Introduction

I.1. Polyimides

Polyimides (Figure I.1) are polymers composed of organic residues linked via cyclic imide functionalities, which are generally derived from the reaction of diamines and dianhydrides. Polyimides can be described as aliphatic, alicyclic, or aromatic and have linear, branched or network structures. In this thesis work, we consider mainly linear aromatic polyimides, as they have found wide practical applications due to their high level of performance over a broad range of temperatures.

Figure I.1. General structure of polyimides.

The first reference to a polyimide was dated at the beginning of the last century.¹ But the actual emergence of polyimides as a polymer class took place in 1955 with a patent of Edwards and Robinson on polyimides from pyromellitic acid and aliphatic diamines.² Since then, interest in polyimides has progressively grown. Due to intensive research done for heat-resistant polymers in the 1960s, polyimides soon became highly important and some polyimides with excellent physical properties have been commercialized (Figure I.2). For example, the most widely used polyimide (Kapton[®]) derived from pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA) exhibits many good properties such as high tensile strength (172.4 MPa), high tensile modulus

(2.1 GPa), outstanding thermal stability (5% weight loss in air at 477 °C), low dielectric constant (3.5 KHz at 25 °C) and excellent solvent resistance.³

Kapton/Dupont

Utem/GE Company

LaRC-TPI/NASA Langley

LaRC-TPI/NASA Langley

PMR-15 composite/NASA

Figure I.2. Commercially available polyimides.

Due to their excellent thermal stability, along with good mechanical and electrical properties, polyimides have found numerous applications as:

- Insulating films, coatings and laminates
- Molded parts

- Structural adhesives
- High-modulus fibres
- High-temperature composites

In addition to these traditional applications, polyimides have also found uses as dielectric insulators and passive layers in the microelectronics industry.

I.2. Synthetic routes to polyimides

I.2.1. Synthesis of aromatic polyimides from dianhydrides and diamines

Two-step method for polyimide synthesis

Two-step polymerization is one of the important methods to prepare polyimides. Usually, a poly(amic acid) is first synthesized from a dianhydride and a diamine in a polar aprotic solvent, such as N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMAc) and N-methylpyrrolidone (NMP) at room temperatures.⁴⁻⁸ Then the poly(amic acid) is dehydrated to the polyimide by extended heating at elevated temperatures or by treatment with chemical dehydrating agents (Scheme I.1). Due to the poor solubilities of polyimides, most of them are usually processed in the form of the poly(amic acid), which is thermally imidized in place.

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

A mechanism that describes the formation of polyimide is shown using a monofunctional species in Scheme I.2. In the first step, nucleophilic attack of the amine groups on the carbonyl groups of the dianhydride leads to the opening of the ring yielding

an intermediate poly(amic acid). In the second step, the poly(amic acid) is converted to the corresponding polyimide through a cyclodehydration reaction.

Scheme I.2. The mechanism of polyimide formation.

The first step is crucial to attain high-molecular-weight chains, and the second one has a great influence on the final nature of the polymer since a quantitative conversion in the cyclodehydration process is needed to have a pure fully cyclized polyimide. The final imidization step can be achieved via two different pathways. The first pathway involves the direct thermal cyclodehydration of the initial poly(amic acid) by heating the system to approximately 300 °C. The thermal imidization of poly(amic acid) represents the most practical approach to imidization, especially for commercial applications. Industrially, thermal processes are most cost-effective and can be readily

instituted and controlled with high precision. The second pathway involves treating the poly(amic acid) with a chemical dehydrating agent such as a mixture of acetic anhydride and pyridine. Although the chemical imidization process is less attractive due to additional expense and process complexity, this approach does offer advantages over the thermal imidization route by eliminating the potential of hydrolytic molecular weight degradation during curing.

One-step method for polyimide synthesis

Polyimides that are soluble in organic solvents are often prepared by the so-called one-step or single-stage method.⁹ Typically, the dianhydride and diamine are stirred in a high boiling organic solvent at 180-220 °C. Under these conditions, chain growth and imidization essentially occur spontaneously. The water generated from imidization is usually allowed to distill off from the reaction mixture. Nitrobenzene, 1-chloronaphthalene and *m*-cresol are the most widely used solvents. Moreover, polyphosphoric acid was also used as a solvent to make polyimides due to its good properties of solubilization and dehydration for many organic compounds. The one-step method is especially useful in the polymerization of unreactive dianhydrides and diamines. Another interesting feature of the one-step method is that it can yield a material with a higher degree of crystallinity than the one obtained from the two-step method. The excellent solvation of the polymer at high temperature may allow it to obtain a more favorable conformation for packing.

1.2.2. Other synthetic routes to polyimides

Aromatic nucleophilic displacement polymerization

Aromatic nucleophilic displacement of bishalo and bisnitro derivatives of aromatic ketones and sulfones with bisphenols afforded poly(ether ketone)s and poly(ether sulfone)s. Poly(ether imide)s were also synthesized by the nucleophilic displacement of bishaloimides¹⁰⁻¹¹ and bisnitroimides¹²⁻¹⁴ with bisphenol salts in dipolar solvents (Scheme I.3). Ultem[®] 1000 resin, manufactured by the General Electric Company, can also be prepared from bisphenol A and *m*-phenylenediamine.

Scheme I.3. Synthesis of polyimides by nucleophilic displacement polymerization.

Polymerization by transimidization

The transimidization reaction of a reactive bisimide with an aromatic diamine is used to prepare polyimides, such as *N,N'*-bis(heteroaryl)bisimides, and high molecular weight poly(ether imide)s were synthesized from these *N,N'*-bis(heteroaryl)bisimides and aromatic diamines (Figure I.3).¹⁵⁻¹⁶

Figure I.3. Structures of *N,N'*-bis (heteroaryl) bisimides.

Polymerization of diisocyanates and dianhydrides

The reaction of anhydrides with isocyanates to give imide was reported by Wurtz in 1854.¹⁷ However, it was not until about 1970 that the reaction found applications in the synthesis of polyimides and copolyimides.¹⁸⁻¹⁹ (Scheme I.4) The reaction of dianhydride with diisocyanate only proceeds at high temperatures such as 180 °C, but in the presence of a catalytic amount of water or alcohol the reaction can readily go at a lower temperature.

Scheme I.4 Synthesis of polyimides from dianhydrides and diisocyanates.

Polymerization of tetracarboxylic acids and their derivatives and diamines

High molecular weight polyetherimides can be made from tetracarboxylic acids and diamines by melt polymerization²⁰ or by a high temperature solution process²¹ (Scheme I.5). It is advantageous to use tetracarboxylic acids instead of dianhydrides to prepare polyimides since moisture-sensitive dianhydrides such as PMDA and BTDA are

difficult to handle, and maintaining purity is a problem. The tetracarboxylic acids are stable and easy to purify.

Scheme I.5. Polymerization of tetracarboxylic acids and diamines.

Self-condensation type monomers can not be isolated because of the high reactivity between anhydride and amino groups. Instead, Nosova *et al.* polymerized aminodicarboxylic acids by a two-step process. Polyamic acid solutions were prepared by the Yamazaki-Higashi phosphorylation method at 60 °C directly from 4-(4-aminophenoxy)phthalic acids (Scheme I.6),²² and high molecular weight polyimides could be obtained from these polyamic acids.

Scheme I.6. Self-condensation of aminodicarboxylic acids.

The derivatives of tetracarboxylic acids such as ester acid chloride or ester acid can also be used to make polyimides. Ding *et al* polymerized diester diacid chloride with an aromatic amine in two steps to obtain a polyimide (Scheme I.7).²³

Scheme I.7. Polymerization of tetracarboxylic acid derivatives and diamines

Some AB or AB₂ type aminodicarboxylic ester acids can be used to prepare linear or hyperbranched polyimides (Scheme I.8).²⁴ The polyimides were prepared from a two-step method in which the direct polycondensation reactions were carried out in NMP in the presence of diphenyl(2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonate (DBOP) as a condensation agent, followed by thermal imidization.

Scheme I.8. Linear or hyperbranched polyimides from AB or AB₂ type monomers.

Polyimides via phthalide derivatives

A new synthetic, low-temperature approach to polyimides has been developed.²⁵ Due to the fact that pyromellitide displays analogous behaviour to pyromellitic dianhydride, it readily reacts with aromatic diamines to form a soluble poly(amic acid)-like intermediate.(Scheme I.9); Unlike poly(amic acid), this intermediate transforms to the polyimide in solution at ambient temperature.

Scheme I.9. Synthesis of polyimides from phthalide derivatives.

Polyimides via high pressure polymerization

Due to the excellent reactivity of nylon-salt-type monomers, high pressure polymerization was used to prepare polyimides. The polymerization was usually performed under 250 Mpa at 200-250 °C for 25 h (Scheme I.10).²⁶

Scheme I.10. Synthesis of polyimides from high pressure polymerization.

Polyimides via metal-catalyzed reaction

Palladium-catalyzed carbonylation and coupling reactions of aromatic dihalides and diamines were also used to make high molecular weight polyimides (Scheme I.11).²⁷ Usually, the reactions performed in either DMAc or NMP at 90-100 °C with 3-6% PdCl_2L_2 ($\text{L} = \text{PPh}_3$) catalyst for 2-6 h at 90 psi CO. The advantage of this route is to afford a fully imidized polymer in one step and at a low temperature. In addition, a variety of monomers can be readily prepared.

Scheme I.11. Synthesis of polyimides by metal-catalyzed reactions.

Polyimides via photochemical polymerization

Based on well-known photoenolization of *o*-methylphenyl ketones, polyimides can be prepared from a 2,5-dibenzoyl-*p*-xylene and a bismaleimide.²⁸ In this approach, photolysis of 2,5-dibenzoyl-*p*-xylene under N_2 using light from a 450 W Hg lamp filtered through Pyrex produces two photoenol moieties, which can afford a polyimide in the presence of a stoichiometric amount of a bismaleimide. This polyimide can be converted into the corresponding anthryl system through dehydration and aromatization process (Scheme I.12).

Scheme I.12. Synthesis of polyimides via photochemical polymerization.

Polyimides via addition polymerization

Monoimides and oligoimides containing unsaturated end groups are susceptible to curing to give a cross-linked or chain-extended polyimides (Scheme I.13) by a radical mechanism or by several other mechanisms, such as photocondensation, Diels-Alder addition, or nucleophilic substitution. Among such end groups are maleimide,²⁹ nadimide,³⁰ acetylene,³¹⁻³² phenylacetylene, biphenylene,³³⁻³⁵ benzocyclobutene,³⁶ allyl,³⁷ and trifluorovinylether³⁸ groups. The introduction of a cross-linking site as an end cap for oligomers is now a general approach to improve the processing and the final properties of aromatic polymers and polyheterocycles, such as PMR polyimides.

Polyimides containing crosslinkable groups such as diacetylene, diphenylacetylene and 1,2-diphenylcyclopropane were also made (Figure I.4).³⁹ After thermal crosslinking, the polyimides had improved solvent resistance and glass transition temperatures.

Scheme I.13. Synthesis of addition polyimides.

Figure I.4. Polyimides containing crosslinkable groups.

I.3. Modifications to polyimides.

Aromatic polyimides were developed in the 1960s, and since then they have been of great technological importance due to their outstanding thermal and electrical properties. However, their applications have been limited in many fields because aromatic polyimides are normally insoluble in common organic solvents and have extremely high glass transition or melting temperatures, which preclude melt processing. This low solubility and poor processability has been proposed to be due to the strong polymer chain-chain electronic interaction occurring between the electron deficient pyromellitimide moieties and the electron rich phenyl rings within the polyimide backbone.⁴⁰ The chain-chain interaction makes the polymer pack extremely well in the solid state. Evidence of this electronic interaction is often seen in enhanced colour of polyimides, such as polyimides made from PMDA and 2,7-diaminofluorenone.⁴¹

A lot of methods have been used to attain solubility in polyimides while maintaining their desirable high temperature characteristics. The majority of approaches have involved the following structural modifications:

- (1) the incorporation of flexible or twisted linkages into the polymer backbone.
- (2) the introduction of pendant substituents along the polymer backbone.
- (3) the disruption of symmetry and recurrence regularity through the copolymerization of two dianhydrides or two diamines.

I.3.1. Soluble polyimides containing flexible or twisted linkages

One of the effective approaches to prepare organo-soluble polyimides is the incorporation of flexible or twisted linkages into the polymer backbone. For example,

highly flexible or twisted aromatic dianhydrides, 3,3',5,5'-tetrabromo-2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl] propane dianhydride,⁴² 4,4'-[sulfonylbis(2,6-dimethyl-1,4-phenylene)dioxy] diphthalic anhydride,⁴³ 2,2'-bis(3,4-dicarboxyphenoxy) biphenyl dianhydride,⁴⁴ 2,2'-bis(3,4-dicarboxyphenoxy) binaphthyl dianhydride,⁴⁵ and 4,4'-(1,4-phenylenedioxy)diphthalic anhydride and its derivatives,⁴⁶ were effectively used to prepare soluble polyimides with various diamines, respectively (Figure I.5). Such aromatic diamines, a,a'-bis[3,5-dimethyl-4-(4-aminophenoxy)phenyl]-1,4-diisopropylbenzene,⁴⁷ 1,2-bis(4-aminophenoxy)-4-*tert*-butylbenzene,⁴⁸ 1,1-bis[4-(4-aminophenoxy)phenyl]-1-phenylethane,⁴⁹ and 6,6'-bis(4-aminophenoxy)-4,4,4',4',7,7'-hexamethyl-2,2'-spirobichroman⁵⁰ were also prepared for the production of soluble aromatic polyimides (Figure I.6).

Figure I.5 Dianhydride containing flexible linkages.

Figure I.6. Diamines containing flexible linkages.

I.3.2. Soluble polyimides containing pendant substituents

Introduction of pendant aromatic side groups into the dianhydrides of the tetracarboxylic acids improves the solubility of the polymer obtained. The polyimides derived from the following 3,5-bis(3, 4-dicarboxybenzoyl) biphenyl dianhydride and its derivative (Figure I.7) are soluble in NMP, DMAc and chlorinated solvents, form flexible strong films from solution, and exhibit no weight loss up to 540 °C.⁵¹⁻⁵²

Figure I.7. Structures of 3,5-bis(3, 4-dicarboxybenzoyl) biphenyl dianhydride and its derivative.

Another organo-soluble polyimides were also made from 5,6-diphenyl-1,2,3,4-tetracarboxylic anhydride.⁵³ (Figure I.8) Due to the twisted pendant phenyl groups and the bent structure of two anhydride groups, the polyimides derived from this dianhydride and other aromatic diamines are also soluble in common organic solvents such as TCE, DMAc, and NMP.

Figure I.8. Structure of 5,6-diphenyl-1,2,3,4-tetracarboxylic anhydride.

Different aromatic diamines containing pendant groups were also made in order to obtain soluble polyimides, for example 3-amino-5-(4-aminophenoxy)diphenyl ether,⁵⁴ diaminotriphenylamine,⁵⁵⁻⁵⁶ tetraphenylthiophenediamine,⁵⁷⁻⁵⁸ 3,3'-benzophenone derivatives,⁵⁹ 4,3'-diamino-2',6'-di(4-biphenyl)-p-terphenyl,⁶⁰ 2',6',3''',5'''-tetraphenyl-4,4''''-diamino-p-quinquephenyl,⁶¹ 4,4'-diamino-2,2'-diphenylbiphenyl, 4, 4''-diamino-2',3',5',6',-tetraphenyl-p-terphenyl,⁶² bis(4-aminophenoxy-3,5-dimethylphenyl)naphthylmethane,⁶³ and 1,4-(4'-aminophenoxy)-2(3'-trifluoromethylphenyl) benzene⁶⁴ (Figure I.9). Recently, another interesting aromatic diamine bearing two generations of Percec-type dendritic blocks was prepared.⁶⁵⁻⁶⁸ The polyimides derived from the dendron-containing diamine were soluble in aprotic polar solvents, however, the improved solubility due to the dendron was not so pronounced as the solubility of the polyamides. The glass transition temperatures of these polyimides were much lower than those similar polyimides without dendron.

The solubilities of polyimides can also be improved by introducing polar substituents into the polyimide backbone. For example, polyimides derived from dianhydride⁶⁹ and diamines⁷⁰⁻⁷¹ containing -OH, -NH₂ or -CN are soluble in NMP, DMF, and DMAc.⁷²⁻⁷³ (Figure I.10) This can contribute to the strong interaction of the hydroxy or amino groups with polar solvents.

Figure I.10. Diamines and dianhydrides containing polar substituents.

I.3.3. Soluble polyimides containing cardo groups

As mentioned before, introducing soft linkages into the polymer backbone increases solubility but lowers rigidity of polymers, which leads to low heat resistance. It is interesting to do structural modifications of polymer backbone that simultaneously increase the solubility and heat resistance of polymers. Introduction of cardo (Latin meaning loop) groups along the polymer backbone has been shown to impart solubility and heat resistance to the resulting polymers.⁷⁴ Many aromatic diamines containing cardo groups have been synthesized, such as 5,5-bis[4-(4-aminophenoxy)phenyl]-4,7-

methanohexahydroindane, 1,1-bis[4-(4-aminophenoxy)phenyl]cyclododecane, 2,2-bis[4-(4-aminophenoxy)phenyl]adamantane, 2,2-bis[4-(4-aminophenoxy)phenyl]norbornane, bis[4-(4-aminophenoxy)phenyl]diphenylmethane, 4,4-bis(p-aminophenoxy)methyl)-1-cyclohexene, and 9,9-bis[4-(4-aminophenoxy)phenyl]fluorene and the polyimides derived from these diamines have increased solubility without sacrificing thermal stability and glass transition temperatures (Figure I.11).⁷⁵

Figure I.11. Structures of various cardo diamines.

The glass transition temperatures of polyimides derived from the cardo diamines and oxydiphthalic anhydride are summarized in Table I.1. According to the contribution

of different cardo groups to increasing thermal stability, they can be arranged in the following order:

It shows that polyimides made from polyalicyclic cardo groups such as adamantane and norbornane-type groups have higher thermal stabilities than those polyimides from alicyclic group like cyclododecane and cyclohexene. Although polyimide I-g had stiff pendant groups, it showed lower T_g than other polyimides. It may be due to the presence of kink unit of the diphenylmethylene group which lowered the rigidity of polymer backbone.

Table I.1. Glass transition temperatures of polyimides (I-a-h).

Polyimides	I-a	I-b	I-c	I-d	I-e	I-f	I-g	I-h
T _g (°C)	274	247	261	276	254	261	248	211

Aromatic dianhydrides containing cardo groups were also prepared, such as bis[4-(3,4-dicarboxy phenoxy)phenyl]diphenylmethane dianhydride, 1,1-bis[4-(4-dicarboxyphenoxy)phenyl]-4-tert-butylcyclohexane dianhydride, 9,9-bis[4-(3,4-dicarboxyphenoxy)phenyl]fluorene dianhydride, and 1,1-bis[4-(3,4-

dicarboxyphenoxy)phenyl]-cyclohexane dianhydride (Figure I.12),⁷⁶ and polyimides derived from these cardo dianhydrides and aromatic diamines were soluble in common organic solvents.

Figure I.12. Structures of aromatic dianhydrides containing cardo groups.

I.3.3. Soluble copolyimides

Soluble polyimides have been made by copolymerizing two different dianhydrides with an aromatic diamine. Similarly, the polymerization of a dianhydride with two diamines or two diisocyanates has afforded soluble polyimides. An example of the effect of copolymerization on solubility is illustrated in the following polyimides I-a-c.⁷⁷ (Table I.2) Polyimide I-b, which was prepared from 100% BPDA, is only soluble in TCE. The 100% PMDA-based polyimide I-c is completely insoluble. However, the copolyimide I-a prepared from 50% of each of these dianhydrides is soluble in amide-like solvents as well as TCE.

Table I.2. Copolyimides I-a-c from two dianhydrides and one diamine.

Polymer	X	Y	Solvents
polyimide I-a	50 %	50 %	DMAc, DMF, TCE
polyimide I-b	100 %	0 %	TCE
polyimide I-c	0 %	100 %	insoluble

Another example of a favorable copolymerization effect is the soluble copolyimide resulting from the polymerization of 80 % of toluene diisocyanate and 20 % of 4,4'-methylenebis(phenyl isocyanate) with PMDA. In this case, the polymers prepared from PMDA and each diisocyanate alone are completely insoluble.⁷⁸

Moreover, alternating copolyimides appeared more soluble than the corresponding random ones, for example the alternating copolyimides in Figure I.13 were soluble in DMF, DMAC, NMP and m-cresol, but the random ones were only soluble in m-cresol.⁷⁹ Apparently, alternate insertion of a bent unit into the rigid polyimide is an effective way to break the rigidity of the polyimide and improve the solubility.

Figure I.13. Structures of alternating copolyimides

I.4. Rationale and Objectives

The demand for use of aromatic polyimides in the aerospace and electronics industries has increased rapidly in recent years due to their excellent thermal stability, mechanical strength and electrical property.⁸⁰⁻⁸² However, the direct use or processing of many polyimides is often limited, due to their relatively poor processability. Moreover, along with the development of information technology (IT), research and development of polyimides are focusing on novel functional materials for microelectronics and photonics fields, such as electrochromic devices, organic transistors, organic light-emitting devices (OLEDs), and polymer-based waveguide components. It is interesting to synthesize new polyimides with improved processability and certain functionalities.

Based on the structure-property relationship of polyimides, two series of organo-soluble polyimides containing naphthalimide moieties are proposed in order to obtain new functional materials (Figure I.14).

Figure I.14. Structure of the naphthalimide moiety.

Accordingly, new dihalide and dianhydride monomers need to be designed for polymerization with various bisphenols and aromatic diamines, respectively. The physical properties of resulting polyimides including electrochemical, electrochromic and optical properties also need to be studied in detail.

I.4.1. Dihalide monomers containing naphthalimide

A series of new dihalide monomers containing the naphthalimide moiety are proposed (Figure I.15). The corresponding poly(ether imide)s can be prepared from the dihalides and bisphenols.

It has been generally recognized that aromatic ether linkages inserted in aromatic main chains provide them with a significantly lower energy of internal rotation.⁸³ In general, such a structural feature leads to significant improvements in solubility but lower glass transition temperatures (T_g) and crystalline melting temperatures (T_m). Since the naphthalimide contains fused aromatic ring, the introduction of naphthalimide moiety into the polymer backbone is expected to improve the thermal stability. Another important feature is the electrochromic properties of naphthalimides. The electrochemical and electrochromic properties of 5 or 6-membered-ring anhydride-based polyimides or related imide compounds have been investigated.⁸⁴ It has been found that the colors of polyimides or imide compounds can be changed due to the electrochemical redox reactions and the reduction potentials for the naphthalimides are lower than that of phthalimides.⁸⁵ In addition to good processability and thermal stability, poly(ether naphthalimide)s derived from the proposed dihalide monomers are expected to be electrochromic with low reduction potentials.

Figure I.15. Designs of new dihalide monomers.

I.4.2. Unsymmetric dianhydride monomer

The symmetric dianhydride monomer BTDA and bis(naphthalic anhydride)s are known to afford polyimides with many excellent thermal and mechanical properties except for solubility.⁸⁶ (Figure I.16) Replacing one of the phenyl ring of BTDA with a 1,4-naphthylene unit will give a new unsymmetric dianhydride. According to structure-property relationships of polyimides, polymers derived from this unsymmetric dianhydride should possess three possible diads in the main chain which lead to a better solubility than the BTDA and bis(naphthalic anhydride)-based polyimides and maintain other desirable properties such as high thermal stability as well as electrochromic property as discussed above. Furthermore, it has been found that naphthalic anhydride does not react with aromatic amine in both protic and aprotic solvents below 140 °C,⁸⁶ so it is possible to control the structures and properties of block copolyimides using this new unsymmetric dianhydride.

Figure I.16. Design of unsymmetric dianhydride monomer.

In summary, the objectives of this thesis work are:

1. To synthesize new dihalide monomers containing naphthalimide moiety and polymerize the dihalide monomers with various bisphenols to form new series of poly(ether naphthalimide)s.
2. To study the electrochemical and electrochromic properties of the poly(ether naphthalimides).
3. To synthesize a new unsymmetric dianhydride monomer and polymerize it with various aromatic diamines to prepare a new series of polyimides and investigate their electrochemical and electrochromic properties.
4. To study the reactivity of different anhydrides in the unsymmetric monomer, and its applications in controlling the structures and properties of copolymers.

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Chapter II

Poly(ether naphthalimide)s

II.1. Introduction

A poly(ether imide) containing flexible ether linkages is more soluble than a rigid rod-like polyimide. The Ultem poly(ether imide) (Figure II.1),¹ for example, exhibits good solubility, thermal stability and good moldability but a relatively lower T_g (215 °C) than most rigid-rod like polyimides.

Figure II.1. Structure of commercial Ultem poly(ether imide).

As mentioned in chapter one, there are two major routes to poly(ether imide)s. One involves the polycondensation of a dianhydride and a diamine and has been used to prepare many poly(ether imide)s. The other route involves nucleophilic reaction of a dihalide and a bisphenol. In this case the dihalide and/or bisphenol monomer must contain an imide moiety and an ether linkage can be easily introduced into polymer backbone. So far, the only two known examples are bis(nitrophthalimide) and bis(4-fluorobenzoyl)phthalimide, which were used as monomers for the synthesis of poly(ether imide)s.¹⁻⁴ In order to prepare poly(ether imide)s containing naphthalimide unit, a series of new dihalides were synthesized (Figure II.2). The dihalide monomers were then polymerized with various bisphenols to obtain new poly(ether imide)s containing

naphthalimide moieties. The introduction of a rigid naphthalene ring into the polymer chain usually leads to an enhanced thermal stability compared to ones with a benzene ring. Therefore, the incorporation of both ether and naphthalene units into a polyimide could result in an increase in solubility, glass transition temperature and thermal stability. In addition to the desired physical properties, the resulting poly(ether naphthalimide)s were also electroactive, as discussed in chapter III.

Figure II.2. Structures of new dihalide monomers.

II.2. Monomer synthesis and characterization

II.2.1. Retrosynthetic analysis

The retrosynthetic analysis for dihalide monomers (II-3) is shown in scheme II.1. The imidization reaction of monohalide containing 6-membered-ring anhydride (II-2) with an aromatic diamine gives dihalide monomer containing naphthalimides. Due to the versatility and availability of diamine, many dihalides can be made in such a way. The key compound II-2 can be prepared through the acylation of acenaphthene with 4-fluorobenzoyl chloride and followed by oxidation.

Scheme II.1. Retrosynthetic analysis for the dihalide monomers.

II.2.2. Synthesis of dihalide monomers

The dihalide monomers II-3a-c were readily synthesized in three steps from acenaphthene, 4-fluorobenzoyl chloride and aromatic diamines in high yields. (Scheme II.2) In the first step, the acylation of acenaphthene with 4-fluorobenzoyl chloride was carried out in dichloromethane in the presence of aluminum chloride. The reaction proceeded in 1 h at 0 °C and produced compound II-1 in 90% yield. Compound II-1 was

then oxidized with $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ in acetic acid to afford 4-(4-fluorobenzoyl)-1,8-naphthalic anhydride (II-2) in 72% yield. Bis(4-fluorobenzoyl)naphthalimides (II-3a-c) were prepared by the condensation of anhydride II-2 with the corresponding diamines according to the conventional imide synthesis method. The difluorides II-3a-c were isolated as yellow solids with melting points typically over 260 °C and used for polymerization without further purification.

Scheme II.2. Synthetic routes to dihalide monomers.

II.2.3. Characterization

The structures of dihalide monomers and intermediates were unambiguously characterized by FTIR, ^1H and ^{13}C NMR and FAB-MS. In their IR spectra, all of the difluoride monomers showed characteristic imide/ketone bands around 1713 and 1665 cm^{-1} . Figure II.3 shows one of the typical IR spectra of dihalide monomer II-3b. The ^1H and ^{13}C NMR data were also consistent with the assigned structures of these difluorides. The ^1H and ^{13}C NMR of dihalide monomer II-3b is shown in Figure II.4 and 5. In ^1H NMR, the signal at 4.23 ppm clearly shows aliphatic protons from methylene group. Due to the complicated splitting patterns, it is difficult to assign the different protons, but the ratio of integration among protons agreed with the structure of dihalide II-3b. In the ^{13}C NMR, there are two carbonyl signals at 164.05 and 163.74 ppm for the naphthalimide and one signal at 194.70 ppm for the ketone. Due to the strong magnetic effect of fluorine, the C_1 , C_2 and C_3 shows split signals. The double peaks at 167.70 and 165.14 ppm are from the C_1 connected with fluorine group and coupling constant is 256 Hz. The results from FAB-MS further confirmed the structures of these dihalide monomers.

Figure II.3 IR spectrum of dihalide monomer II-3b.

Figure II.4. ^1H NMR spectrum of dihalide monomer II-3b.

Figure II.5. ^{13}C NMR spectrum of dihalide monomer II-3b.

II.3. Polymer synthesis and characterization

II.3.1. Synthesis

The poly(ether naphthalimide)s II-4a-i were obtained by polymerization reaction of bis(4-fluorobenzoyl)naphthalimides II-3a-c with three different bisphenols, i.e. 4,4'-(isopropylidene)diphenol (BPA), 4,4'-(hexafluoroisopropylidene)diphenol (6F-BPA), and 9,9'-bis(4-hydroxyphenyl)fluorene (FBP) (Scheme II-3). All of the Polymerizations were done in DMAc with toluene as an azeotroping agent using stoichiometric amounts of the dihalide and bisphenol monomers in the presence of potassium carbonate. During the initial stage of polymerization, the reaction temperature was maintained at approximately 140 °C and the water generated from the bisphenoxide formation was removed azeotropically through a Dean-Stark trap. Upon the complete formation of a bisphenoxide (1-2 h), the polymerization temperature was increased to 160 °C to effect the displacement reaction. A high molecular weight polymer was obtained within 3 h as judged by a dramatic increase in solution viscosity and the GPC results. The resulting polyimide was isolated and washed thoroughly with methanol and boiling water to remove any inorganic salts.

The same polymerization procedure was applied to three difluoride monomers (II-3a-c) cross-coupled with three bisphenols (BPA, 6FBPA, FBP), affording three series of polyimides or a total of nine polyimides, II-4a-c, 4d-f and 4g-i. Transparent and tough film could be cast from the polymer solution.

Scheme II.3. Synthesis of poly(ether imide)s (II-4a-i).

II.3.2. Characterization

All polymers were obtained as off-white, fibrous solids. The IR spectra of these polyimides showed a characteristic band at 1239 cm⁻¹, indication of the ether formation. The two bands due to the naphthalimide moiety were at 1714 and 1672 cm⁻¹. Most polymers were soluble in DMAc, N-methyl-2-pyrrolidone (NMP), N,N-dimethylformamide (DMF), and 1,1,2,2-tetrachloroethane (TCE) (Table II.1). Except for polymers II-4a-c derived from *p*-phenylenediamine that were partially soluble in

chloroform, all the other polymers (II-4d-i) were also readily soluble in chloroform at ambient temperatures. Nevertheless, the solubility of poly(ether naphthalimide)s was found to be comparable to Ultem poly(ether imide), which is soluble in polar aprotic solvents and chlorinated solvents.

Table II.1. Solubilities of polyimides II-4a-i.

Polymer II-4a-i	Solvent ^b					
	THF	CHCl ₃	TCE	DMAc	DMF	NMP
4a(3a+BPA)	–	±	+	+	+	+
4b(3a+6FBPA)	–	±	+	+	+	+
4c(3a+FBP)	–	±	+	+	+	+
4d(3b+BPA)	–	+	+	+	+	+
4e(3b+6FBPA)	–	+	+	+	+	+
4f(3b+FBP)	–	+	+	+	+	+
4g(3c+BPA)	–	+	+	+	+	+
4h(3c+6FBPA)	–	+	+	+	+	+
4i(3c+FBP)	–	+	+	+	+	+

^a +: soluble, ±: partially soluble, -: insoluble

^b THF: tetrahydrofuran; TCE: 1,1,2,2-tetrachloroethane; DMF: N,N-dimethylformamide; NMP: 1-methyl-2-pyrrolidinone.

II.3.3. Molecular weights

Gel permeation chromatography (GPC) was used to measure the molecular weights of polymers II-4a-i relative to polystyrene standards (Table II.2). GPC results showed that all of the polymers were of high molecular weight. Molecular weights (M_w) ranged from a minimum of 4.67×10^4 for the II-3b/BPA based polymer to a maximum of 33.86×10^4 for the II-3c/FBP based polymer, and the M_w/M_n ratio is in the range of 1.25 to 2.04. The inherent viscosities of polymers II-4a-i also supported the GPC results with

a range from 0.31 to 1.04 dL/g, indicating the formation of high molecular weight polymers.

Table II.2. Molecular weights and inherent viscosities of polyimides II-4a-i.

Polymers	Monomers used	η_{inh}^a (dL/g)	M_w^b ($\times 10^{-4}$)	M_n^b ($\times 10^{-4}$)	M_w/M_n
II-4a	II-3a/BPA	0.54	6.78	4.41	1.54
II-4b	II-3a/6FBPA	0.58	8.14	4.97	1.63
II-4c	II-3a/FBP	0.54	6.88	4.90	1.41
II-4d	II-3b/BPA	0.31	4.67	3.77	1.25
II-4e	II-3b/6FBPA	0.32	6.16	4.54	1.36
II-4f	II-3b/FBP	0.76	7.87	4.19	1.88
II-4g	II-3c/BPA	0.45	9.23	4.92	1.88
II-4h	II-3c/6FBPA	0.79	18.09	9.83	1.84
II-4i	II-3c/FBP	1.04	33.86	16.49	2.05

^a Inherent viscosity in chloroform at 25 °C

^b Determined by GPC relative to polystyrene standards.

II.3.4. Polymer properties

The glass transition temperatures (T_g) were determined by differential scanning calorimetry (DSC) at a heating rate of 10 °C/min under an atmosphere of nitrogen. The T_g values of these poly(ether naphthalimide)s (II-4a-i) ranged from 283.0 to 341.6 °C, depending on the difluoride monomers and bisphenols used (Table II-3). Among all the synthesized polyimides, polyimide II-4c showed the highest T_g of 341.6 °C, which can be attributed to the rigid *p*-phenylene unit and the bulky cardo group in the polymer backbone. Polyimide II-4d and II-4g had relatively lower T_g (283 °C) due to the presence of extra flexible methylene and isopropylidene units. As expected, the T_g

values of all the poly(ether naphthalimide)s synthesized were higher than that (215 °C) of Ultem poly(ether imide). The effect of the rigid naphthalimide moiety on the Tg could be seen by comparing polymers II-4a, II-4d and II-4g with Ultem poly(ether imide), since they all have the BPA moiety. Moreover, the Tg was also affected by the bisphenol unit incorporated in the polyimides, as the polyimides II-4c, II-4f and II-4i derived from bulky FBP had relatively higher Tg values than others.

In addition, these poly(ether naphthalimide)s exhibited a good thermal stability, the decomposition temperatures as assessed by the onset temperature (Td) of 5% weight loss by TG occurred in the range of 448-498 °C in nitrogen (Table II.3).

Table II.3. Thermal properties of polyimides II-4a-i.

Polyimides	Monomers used	Tg, ^a (°C)	Td, ^b (°C)
II-4a	II-3a/BPA	300.0	484.6
II-4b	II-3a/6FBPA	304.6	449.5
II-4c	II-3a/FBP	341.6	461.9
II-4d	II-3b/BPA	283.0	456.5
II-4e	II-3b/6FBPA	289.6	474.0
II-4f	II-3b/FBP	321.2	448.5
II-4g	II-3c/BPA	283.3	449.8
II-4h	II-3c/6FBPA	299.8	498.0
II-4i	II-3c/FBP	314.2	448.4

^a Determined by DSC at a heating rate 10 °C/min in nitrogen (100 mL/min).

^b Temperature for 5% weight loss determined by TGA at a heating rate 10 °C/min in nitrogen (200 mL/min).

II.3.5. Comparison of poly(ether naphthalimide)s with their analogues

A series of poly(ether imide)s with similar structures to polymers II-4a-i were synthesized (Figure II.6).³ In order to further investigate the effect of naphthalimide unit on the properties of polymer, the T_g and solubilities of both series of polymers are listed in Table II.4. In each case, naphthalimide-based polymer causes an increase in T_g compared to phthalimide-based analogue and the increases in T_g are significant (>66 °C). The increased T_g is apparently due to the fused naphthalene ring. The solubilities of the resulting polymers are also improved such as polymer II-4d which is soluble in CHCl₃, but its analogue II-5d only swell in CHCl₃. Clearly, it is because of the effective disruption to chain packing imposed by the naphthalene unit.

Figure II.6. Structures of naphthalimide and phthalimide-based polymers.

Table II.4. Comparison of polymer II-4d,4g with their analogues II-5d, 5g.

Polymer	T _g (°C)	Solubility	
		CHCl ₃	DMAc
II-4d	283	+	+
II-5d	216	swell	+
II-4g	283	+	+
II-5g	217	+	+

* + : soluble

II.4. Conclusions

A series of difluoride monomers II-3a-c containing naphthalimide units were successfully synthesized in three steps from acenaphthene and 4-fluorobenzoyl chloride in 65% overall yield. Polymerization of these dihalide monomers with three bisphenols produced a new series of poly(ether imide)s II-4a-i containing the naphthalimide units in the main chain.

In all cases, incorporation of the naphthalimide moiety into poly(ether imide)s can stiffen the polymer backbone, as evidenced by increases in T_g , relative to its phthalimide equivalent, and at the same time maintain a high thermal stability and a good solubility. The onset temperatures for 5% weight loss for the polymers II-4a-i was over 448 °C, as assessed by thermogravimetry at a heating rate of 10 °C/min in nitrogen.

II.5. Experimental section

Materials

Acenaphthene was recrystallized from ethanol. 4,4'-Isopropylidenediphenol (BPA), 4,4'-(hexafluoroisopropylidene)diphenol (6FBPA) and 9,9-(4-hydroxyphenyl)fluorene (FBP) were recrystallized from toluene. 4-Fluorobenzoyl chloride, dichloromethane, anhydrous aluminum chloride, sodium dichromate dihydrate, 4,4'-oxydianiline, 4,4'-diaminodiphenylmethane, *p*-phenylenediamine, *m*-cresol and isoquinoline were purchased from Aldrich Chemical Co. and used without purification. N, N-Dimethylacetamide (DMAC) was vacuum distilled from CaH₂. Other solvents were used as received.

Measurements

The ¹H- and ¹³C-NMR spectra were recorded on either a Varian Gemini-200 or a Bruker-400 instrument using tetramethylsilane as an internal reference. Infrared measurements were performed on a Bomen Michelson 120 FTIR spectrometer. Low-resolution mass EI and FAB spectra were obtained on VG7070E and Kratos Concept 2H spectrometers, respectively. Melting points were taken on a Fisher-Johns melting apparatus or on a Seiko 220C differential scanning calorimeter (DSC) at a heating rate of 10 °C/min in nitrogen (100 mL/min). The apparent molecular weights of the polymers were determined by gel permeation chromatography (GPC) relative to polystyrene standards using chloroform at ambient temperature at a flow rate of 1.0 mL/min; an UV detector was set at 254 nm. Inherent viscosities were measured at a concentration of 0.5 g/dL in chloroform at 25 °C using an Ubbelohde dilution viscometer. The glass

transition temperatures were determined on a Seiko 200 °C DSC at a heating rate of 10 °C/min in nitrogen (100 mL/min). In all cases, the midpoint of change in the slope of the base line from second scan was taken as the T_g . Thermal stabilities, as measured by weight loss, of the polymer samples were determined using a Seiko 120TG /DTA analyzer from 25 to 600 °C at a heating rate of 10 °C/min in nitrogen (200 mL/min).

Monomer Synthesis

4-(4-Fluorobenzoyl)-1,8-naphthalic anhydride (II-2)

In a flask equipped with a condenser, a nitrogen gas inlet and a stirrer, acenaphthene (20.00 g), 4-fluorobenzoyl chloride (20.56 g) and dichloromethane (200 mL) were placed. Anhydrous aluminum chloride (20.75 g) was then added slowly to the solution with simultaneous cooling to maintain a temperature of 0 °C. After 1 h the reaction temperature was allowed to gradually rise to room temperature and the mixture was poured onto crushed ice. The organic layer was separated and dried over anhydrous magnesium sulfate. On removal of dichloromethane, the ketone II-1 was obtained, purified by recrystallization from ethanol and then treated with $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ (100 g) in acetic acid (500 mL) for 4 h at 100 °C. The reaction mixture was poured into water (1 L) and the resulting precipitate was filtered and washed with water and acetic acid. The anhydride II-2 was dried in oven at 100 °C overnight and then recrystallized from acetic

anhydride: 29.91 g (72 %); mp 218-220 °C; MS (EI, m/e , relative intensity %) 320 (M^+ , 100); IR (KBr) 1773, 1738 and 1658 cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, $\text{CDCl}_3/\text{CF}_3\text{COOD}$) δ 8.76 (d, 2 H, $J = 7.52$ Hz), 8.43 (dd, 1 H, $J = 8.56, 3.8$ Hz), 7.95-7.89 (m, 4 H), 7.28-7.22 (m, 2 H); $^{13}\text{C-NMR}$ (100 MHz, $\text{CDCl}_3/\text{CF}_3\text{COOD}$) δ 195.75, 168.36, 165.78, 161.03, 160.75, 143.15, 134.75, 133.71, 133.66, 133.61, 132.68, 132.55, 132.53, 130.61, 129.37, 129.01, 127.64, 120.24, 118.52, 116.72, 116.49 (d, $^2J_{\text{C-F}} = 258$ Hz).

Difluoride II-3a

In a 250 mL three-necked, round-bottomed flask equipped with a magnetic stirrer, a nitrogen inlet and a Dean-Stark trap fitted with a condenser, anhydride II-2 (16.00 g, 0.050 mol), *p*-phenylenediamine (2.70 g, 0.025 mol), *m*-cresol (80 mL) and isoquinoline (2 mL) were placed. The reaction mixture was stirred at 200 °C for 4 h. After cooling to room temperature, the solution was poured into 500 mL of methanol. The solid II-3a was collected and washed with methanol: 16.91 g (95 %); mp 289-290 °C; MS (FAB, relative intensity %) 713 ($M+H^+$, 1.2); IR (KBr) 1713 and 1661 cm^{-1} (imide and C=O); $^1\text{H-NMR}$ (400 MHz, $\text{CDCl}_3/\text{CF}_3\text{COOD}$) δ 8.83-8.80 (m, 4 H), 8.42 (dd, 2 H, $J = 8.52, 0.96$ Hz), 7.99-7.90 (m, 8 H), 7.61 (s, 4 H), 7.28-7.23 (m, 4 H); $^{13}\text{C-NMR}$ (100 MHz, $\text{CDCl}_3/\text{CF}_3\text{COOD}$) δ 197.74, 168.75, 166.16, 165.45, 165.03, 142.61, 135.14, 134.10,

134.00, 133.78, 133.20, 132.62, 132.60, 131.63, 130.17, 129.35, 128.88, 127.66, 123.98, 122.04, 116.82, 116.60 (d, $^2J_{C-F}$ = 259 Hz).

Difluoride II-3b

Difluoride II-3b was obtained in 96% yield from reaction of anhydride II-2 (16.00 g, 0.050 mol) and 4,4'-diaminodiphenylmethane (4.950 g, 0.025 mol) in 80 mL of *m*-cresol and 2 mL of isoquinoline at 200 °C for 4 h. mp 274-275 °C; MS (FAB, relative intensity %) 803 (M+H⁺, 9.6); IR (KBr) 1713 (imide) and 1670 cm⁻¹ (imide and C=O); ¹H-NMR (400 MHz, CDCl₃) δ 8.38 (dd, 2 H, J = 8.52, 0.96 Hz), 7.95-7.80 (m, 8 H), 7.47 (d, 4 H, J = 8.28 Hz), 7.33-7.18 (m, 8 H), 4.23 (s, 2 H); ¹³C-NMR (100 MHz, CDCl₃) δ 194.70, 167.70, 165.14, 164.05, 163.74, 141.92, 141.12, 133.45, 133.43, 133.23, 133.14, 132.19, 132.04, 130.25, 130.20, 129.42, 128.89, 128.60, 128.16, 127.19, 124.70, 123.12, 116.30, 116.08, 41.25 (d, $^2J_{C-F}$ = 256 Hz).

Diffluoride II-3c

Dihalide II-3c was obtained in 90% yield from reaction of anhydride II-2 (16.00 g, 0.050 mol) and 4,4'-oxydianiline (5.00 g, 0.025 mol) in 80 mL of *m*-cresol and 2 mL of isoquinoline at 200 °C for 4 h. mp 262-263 °C; MS (FAB, relative intensity %) 805 ($M+H^+$, 69.2), IR (KBr) 1712 and 1671 cm^{-1} (imide and C=O); $^1\text{H-NMR}$ (400 MHz, $\text{CDCl}_3/\text{CF}_3\text{COOD}$) δ 8.81 (d, 4 H, $J = 7.52$ Hz), 8.42 (d, 2 H, $J = 8.56$ Hz), 7.97-7.88 (m, 8 H), 7.38-7.21 (m, 12 H); $^{13}\text{C-NMR}$ (100 MHz, $\text{CDCl}_3/\text{CF}_3\text{COOD}$) δ 196.08, 168.22, 165.65, 165.43, 165.05, 157.61, 144.14, 142.61, 133.67, 133.57, 133.47, 133.05, 132.88, 132.86, 131.39, 130.01, 129.31, 129.24, 128.83, 128.63, 127.47, 123.86, 122.18, 120.23, 116.61, 116.39 (d, $^2J_{\text{C-F}} = 257$ Hz)

Polymerizations

All the poly(ether naphthalimide)s were prepared by the reaction of bisphenols and difluoride monomers in the presence of potassium carbonate in DMAc at 160 °C. A typical polymerization is as follows: To a 100 mL three-necked, round-bottomed flask fitted with a stirrer, nitrogen gas inlet and Dean-Stark trap with a condenser, were added II-3a (5.0000 g, 0.0070 mol), 4,4'-isopropylidenediphenol (1.6011 g, 0.0070 mol), potassium carbonate (1.1629 g, 0.0084 mol), DMAc (33 mL) and toluene (10 mL). The

mixture was heated to reflux (e.g., 140 °C), and water was removed by azeotropic distillation with toluene for 1-2 h. The reaction temperature was then held at 160 °C for 3 h. After cooling to room temperature, the reaction solution was diluted with an equal volume of DMAC and filtered through a pad of celite to remove inorganic salts. The polymer solution was then coagulated in methanol and then in boiling water for 1 h. Polymer II-4a (6.27 g, 95%) was then dried in a vacuum oven at 140 °C overnight.

II.6. References

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Chapter III

Electrochemical and Electrochromic Properties of Poly(ether naphthalimide)s

III.1. Introduction

Polymeric materials capable of undergoing a reversible electrochemical reduction/oxidation process are currently of interest in connection with electrochromic displays,¹ light-emitting electrochemical cells,² and solid-state batteries.³ Electrically conducting polymers such as polythiophene, polypyrrole, polyaniline and their derivatives are under extensive investigation as electrochromic materials because of the advantages they offer in tailorability of colour and processability. Most of these polymers are anodically colouring materials and undergo a reversible p-doping-undoping process, which involves anion transport in and out of the polymer matrix to balance the electronic charge. Some conjugated polymers also undergo an n-doping process with cation insertion to balance the injected charge and are potentially cathodically coloring materials. However, the study on n-doping polymers is rather limited. The polythiophene derived from 3,4-ethylenedioxythiophene (Baytron P from Bayer Inc.)^{4,5} is one of a few cathodically colouring polymers.

Polyimides are widely used in the electronics industry owing to their excellent chemical, thermal and dielectric properties.⁶ Following the early studies by Haushalter and Krause,⁷ the redox properties of various imides and polyimides have been described.⁸⁻¹⁰ But their electrochromic properties have been scarcely investigated. Most imide compounds and polyimides studied so far contain a diimide unit, in which the two

identical imide groups are attached symmetrically to an aromatic core. These diimides undergo a typical redox process involving the formation of a radical anion upon the first reduction and a dianion upon the second reduction.⁸⁻¹⁰ Regarding the electrochromic behaviour, it has been confirmed that the formation of a radical anion results in a bathochromic shift in the visible region. But the formation of the dianion causes a hypsochromic shift, due to the fact that the additional energy generated from the electron spin pairing for the dianion HOMO excites an electron to the next highest level.¹⁰ This hypsochromic shift also reflects the loss of aromaticity in the benzene ring as the quinoid character increases. Since the difference between the first and second reduction potentials for these known diimides is usually rather small, the electrochemical control of a reversible high-contrast coloration at two distinct wavelengths or between the neutral state and the radical anion would be extremely difficult.

Viehbeck and co-workers investigated the structural effect of aromatic imides on the reduction potentials and UV-Vis absorption.¹⁰ Their study showed that the electrochemical reduction was facilitated with an increase in electron deficiency of an aromatic imide. For example, a naphthalene-1,4,5,8-tetracarboxylic diimide has a lower reduction potential than that of a naphthalimide and the latter is less colored than the former in the neutral state. Therefore, to have a colorless imide or polyimide with a low reduction potential, one would need to incorporate a strong electron-withdrawing group that does not cause an increase in absorption in the visible spectral region. The synthesis of a new class of poly(ether naphthalimide)s with good thermal stability and solubility was reported in chapter 2 (e.g., polyimide III-5, Figure III.1).¹¹ The electron-withdrawing carbonyl group on the naphthalimide ring should be able to enhance the

imide reactivity towards electrochemical reduction. Thus, such a substituted naphthalimide may serve as an electrochromic material with desired properties such as low redox potential and high-contrast coloration. In this chapter, the study on the electrochemical and electrochromic properties of polyimide III-5 as well as the related compounds was conducted. The feasibility of these compounds to undergo n-doping process was confirmed. Importantly, based on their unique structure of the isolated (non-conjugated) imide groups and the introduction of a ketone group to polymer chain, the simple electrochromism (i.e. absorbance peaks shift to high wavelengths upon the increase of reduction degree and vice-versa) has been achieved. Furthermore, these n-doping polyimides will be useful as cathodically coloring materials for the development of all polymer electrochemical displays by coupling with other appropriate p-doping conducting polymers.

III.2. Electrochemistry of polyimides

III.2.1. Electrochemistry of model compounds

In order to correlate the functional groups in the polyimide III-5 with its electrochemical behavior, cyclic voltammetry of model compounds III-1-4 was first investigated. The structures of the model compounds and polymer are shown in Figure III.1.

Figure III.1. Structures of model compounds III-1-4 and polyimide III-5

The reversible and stable cyclic voltammograms were obtained for compounds III-1-4 in DMF containing 0.1 M $n\text{-Bu}_4\text{NClO}_4$. The voltammetric data are listed in Table III.1.

Table III.1. Cyclic voltammetric data for model compounds III-1-4 and polyimide III-5.^a

Model/polymer	Epc ₁ /Epa ₁ (V)	ΔEp ₁ (V)	Epc ₂ /Epa ₂ (V)	ΔEp ₂ (V)	Epc ₁ -Epc ₂ (V)
III-1	-1.31/-1.19	0.12	-	-	-
III-2	-	-	-1.68/-1.41	0.27	-
III-3	-0.88/-0.64	0.24	-1.30/-1.06	0.24	0.42
III-4	-0.79/-0.63	0.15	-1.21/-1.16	0.15	0.42
III-5	-0.82/-0.66	0.16	-1.21/-1.08	0.13	0.39

^a Electrolyte solution: 0.1 M n-Bu₄NClO₄ in DMF; Scan rate: 100 mV/s.

For comparison, cyclic voltammograms of model compounds III-1-4 are shown in Figure III.2.

As shown in Figure III.2, naphthalimide III-1 displayed a pair of reversible peaks at -1.31 V (Epc₁) and -1.19 V (Epa₁). The observed electrochemical reduction of the imide compound is the same as reported previously,⁸⁻¹⁰ confirming the imide's carbonyl group as the electroactive site and its electron affinity as responsible for the n-doping electrochemical process. Nevertheless, it was noticed that, unlike the symmetric aromatic diimide compounds, where two pairs of peaks are always observed, compound III.1 displayed a pair of peaks only. Obviously, the structure difference between a single imide and a diimide does play an important role in determining their distinct electrochemical behavior.

One pair of reversible peaks was also observed for ketone III-2, showing that the carbonyl group also undergoes a reversible electrochemical redox reaction. The reduction of ketone III-2 occurred at a more negative potential than imide III-1 (Table III.1 and Figure III.2), as clearly indicates that the reduction potential relates to the electron affinity of the carbonyl group. Accordingly, two pairs of reversible peaks

appeared for the keto imide III-3 (Figure III.2), which can be assigned to reductions of the imide ($E_{pc1} = -0.88$ V) and ketone ($E_{pc2} = -1.30$ V) groups. A shift of the two reduction peaks for compound III-3 to the less negative potential region can be attributed to the electron-withdrawing effect of the ketone and imide groups on each other. Compound III-4, a representative dimer of compound III-3, displayed the same two pairs of redox peaks as compound III-3. Based on the observation for model compounds III-1-3, the two-step reduction process observed in compound III-4 can be assigned to the reduction of imide and ketone groups, respectively. It is interesting to note that the peak separations of both imide (ΔE_{p1}) and ketone (ΔE_{p2}) groups of compound III-4 are nearly half of those of the corresponding groups in compound III-3. According to the inversely proportional relationship between peak separation (ΔE) and the number of electron (n) transferred during redox process,¹² it clearly shows that the numbers of electrons gained during the reduction of compound III-4 are respectively twice those of the corresponding functional groups of compound III-3. This strongly indicates that the two imide groups or the two ketone groups in compound III-4 are concurrently reduced, as the result of breaking the π -conjugation between two naphthalimide units by the oxydiphenylene group. Thus, the redox behavior of compound III-4 is unique and different from that reported previously for conjugated aromatic diimides and related polyimides such as pyromellitimides and naphthalene-1,4,5,8-tetracarboxylic diimides,⁸⁻¹⁰ where the two pairs of typical redox peaks are due to the successive reduction of two conjugated imide groups.

Figure III.2. Cyclic voltammograms of model compounds III-1-4 obtained at platinum electrode in DMF. Electrolyte: 0.1 M $n\text{-Bu}_4\text{NClO}_4$. Scan rate: 100 mV/s.

According to above electrochemical studies, a different redox process is proposed for this type of polyimides (Scheme III.1). The first electron reduces the neutral naphthalimide **A** to the corresponding radical anion **B**, which upon receiving another electron by the carbonyl group yields the dianion **C**.

Scheme III.1. Proposed two-step redox reactions for model compound III-3.

III.2.2. Electrochemistry of polyimide

Since polyimide III-5 was made from compound III-4, its electrochemical behavior should be similar to that of its monomer. Indeed, by comparing the redox potentials, peak separations (ΔE) of both imide and ketone groups as well as the difference between the reduction of imide and ketone groups ($\Delta E_{p1} - \Delta E_{p2}$), compound III-4 and polyimide III-5 showed similar electrochemical behaviors in solution. The cyclic voltammogram of polyimide III-5 in DMF solution is shown in Figure III.3.

Figure III-3. Cyclic voltammogram of polyimide III-5 obtained at platinum electrode in DMF. Electrolyte: 0.1 M $n\text{-Bu}_4\text{NClO}_4$. Scan rate: 100 mV/s.

The electrochemical study on polyimide III-5 in the solid state was then performed. The cyclic voltammetry of the polymer-coated electrode was carried out in propylene carbonate (PC) containing 0.1 M $n\text{-Bu}_4\text{NClO}_4$. Two pairs of reversible peaks ($E_{pc1} = -0.97$ V, $E_{pc2} = -1.27$ V) were observed (Figure III.4).

Figure III.4. Cyclic voltammogram of polyimide III-5-coated platinum electrode in propylene carbonate. Electrolyte: 0.1 M $n\text{-Bu}_4\text{NClO}_4$. Scan rate: 100 mV/s.

In order to compare with the results obtained in solution (Figure III.3), the silver reference electrode was calibrated using ferrocene in PC and DMF solution containing 0.1 M $n\text{-Bu}_4\text{NClO}_4$. The E_{pc} of ferrocene in PC and DMF are 0.28 V and 0.31V, respectively. By calculation, a slightly negative shift of potentials was expected for the reduction of both imide and ketone groups of polyimide III-5 in the solid state due to slower transport of compensating ions within the polymer network. The polymer film was also stable upon potential cycling within the studied 800 cycles (Figure III.5). This stability is a desirable property for the future application in electrochemical devices.

Figure III.5. Cyclic voltammogram of polyimide III-5-coated platinum electrode in propylene carbonate at different scans. Electrolyte: 0.1 M $n\text{-Bu}_4\text{NClO}_4$. Scan rate: 100 mV/s.

The effects of electrolyte concentration and composition on the electrochemical behavior of polyimide III-5 were also investigated. It was found that, when the concentration of $n\text{-Bu}_4\text{NClO}_4$ increased from 0.001 M to 1.0 M, the redox potentials shifted anodically, indicating that cation insertion/deinsertion is responsible for the electro-neutrality during the redox process. The composition of the electrolyte solution was also found to be another important factor governing the electrochemical response. In the solution containing $n\text{-Bu}_4\text{NClO}_4$ or Et_4NClO_4 as a supporting electrolyte, no difference in electrochemistry was found. But poor electrochemical responses were observed in solutions containing an inorganic electrolyte such as LiClO_4 , NaClO_4 or

KClO₄. Once again, it was confirmed that larger cations facilitate the imide reduction due to the enhanced solvophobic interactions.¹³

Moreover, the redox potentials were found to be independent of potential scan rate (ν), while the redox currents increased as the scan rate increased. (Figure III.6) This phenomena may be due to very fast electron transfer rate (reversible rate). The current maxima of reduction peak according to the square root of scan rate (ν) is linear in the range of 10 ~ 100 mV/s, indicating that the redox process is kinetically controlled by the diffusion process and the insertion/desertion of cations for achieving electroneutrality dominantly determines the redox process of polyimide III-5.^{14,15}

Figure III.6. Plots of peak current maxima vs. $\nu^{1/2}$ for first reduction (circles) and second reduction (solid squares) of polyimide III-5 coated Pt electrode in 0.1 M Bu₄NClO₄ in propylene carbonate.

III.3. Electrochromic properties of polyimides

The electrochromic property of polyimide III-5 was then studied by applying a range of negative potentials on the polymer-coated ITO glass electrode. It was found that the color of polymer film was greatly affected by the degree of reduction. Figure III.7 shows the *in-situ* UV-Vis spectra for polyimide III-5 at different redox states.

Figure III.7. *In-situ* UV-Vis spectra of polyimide-5-coated ITO glass electrode in propylene carbonate containing 0.1 M $n\text{-Bu}_4\text{NClO}_4$. (a) 0.0 V, (b) -1.1 V, (c) -1.3 V, (d) -1.8 V.

At 0.0 V, the polymer film is nearly colorless with a maximum absorption at 342 nm. When the applied potential decreased to -1.1 V, the intensity of this band decreased and the polymer film turned to red with the appearance of new peaks at 483 and 850 nm and two shoulder peaks at 426 nm and 512 nm. The intensity of these new absorption bands decreased with further decrease of the applied potential to -1.8 V. The polymer

film became dark blue with the occurrence of two major absorption bands at 368 and 648 nm and a shoulder peak at 605 nm. The intensity of these new bands increased concurrently with the decrease of the 483 and 850 nm bands. A tight isosbestic point was found at 417 nm for gradual conversion from a radical anion to a dianion (Figure III.7, spectra b, c and d). It is clear that the band at 342 nm corresponds to the π - π^* electronic transition and the bands at 483 and 850 nm belong to the electronic transition of the radical anion. As shown in Figure III.7, polyimide III.5 does not have any absorption in the near infrared (NIR) region at the neutral state. When applying a potential of -1.1 V, the polymer shows a broad absorption with a maximum at 850 nm due to the π -stacking (e.g., a dimer) of the radical anion within the polymer film.^{16,17} With further decrease of a potential to -1.8 V, this NIR band disappeared, indicating the complete formation of a dianion species.

It should be noted that for model compound III-4 and polyimide III-5 studied in this work, the fully reduced dianion species consist of the imide and ketone groups, rather than a dianion of the two imides as in the case for the conjugated diimides. As being reduced gradually, polyimide III-5 becomes darker without a reversed shift of the visible chromophore as seen for naphthalene-1,4,5,8-tetracarboxylic diimides and related polyimides.¹⁰

III.4. Conclusions

The poly(ether naphthalimide)s are electroactive and the electroactive sites within the polymer were identified to be the ketone and imide groups. The stepwise coloration process, colorless – red – dark blue corresponding to the neutral, radical anion and dianion species, was found to be related to the first reduction of the imide group and the second reduction of the ketone group. Based on this new polyimide a high-contrast switch between colorless and red or colorless and dark blue can be achieved and controlled electrically.

III.5. Experimental section

Materials

1,8-Naphthalic anhydride, n-hexylamine, acetonitrile (AN), N,N'-dimethylformamide (DMF), propylene carbonate (PC) and 1,1,2,2-tetrachloroethane (TCE) were purchased from Aldrich Chemical Co. and used as received. Supporting electrolytes, tetra-n-butylammonium perchlorate (n-Bu₄NClO₄), tetraethylammonium perchlorate (Et₄NClO₄), lithium perchlorate (LiClO₄), sodium perchlorate (NaClO₄) and potassium perchlorate (KClO₄) were purchased from Fluka, Aldrich and Sigma and used without further purification. All other chemicals were reagent grade unless otherwise stated. Indium tin oxide (ITO) coated glass were purchased from Delta Technologies Ltd.

Measurements.

The ¹H and ¹³C NMR spectra were recorded on either a Varian Gemini-200 or a Bruker-400 instrument using tetramethylsilane as internal reference. Infrared measurements were performed on a Bomem Michelson 120 FTIR spectrometer. Melting points were taken from a Fisher-Johns melting apparatus or from a Seiko 220C differential scanning calorimeter (DSC) at a heating rate of 10 °C/min in nitrogen (200 mL/min).

Electrochemical measurements were performed using a BAS 100B/W electrochemical workstation interfaced and monitored with a PC computer. The three-electrode system was employed throughout this work, which consists of a working

electrode, a silver wire reference electrode and a platinum wire auxiliary electrode. The platinum disc electrode ($s = 0.018 \text{ cm}^2$) for cyclic voltammetry and ITO coated glass electrode ($0.5 \times 2.5 \text{ cm}^2$) for UV-Vis spectrophotometry were used, respectively. In all cases, the electrolyte solutions were deoxygenated with nitrogen for 10 min prior to use.

Spectroelectrochemical measurements were carried out by combining electrochemical workstation with a Perkin-Elmer Lambda 900 Spectrophotometer and using a quartz cuvette cell containing an ITO working electrode, a platinum wire auxiliary electrode and a silver wire reference electrode. A blank ITO glass electrode with the electrolyte solution was used as reference.

Preparation of polymer-coated electrodes

A solution for polymer III-5 in TCE (25.0 mg/mL) was drop cast or spin coated onto a platinum disc electrode or ITO glass electrode and then dried in an oven at 80°C for 10 min.

Model compounds and polymer

The synthesis method of model compounds III-2-4 and polyimide III-5 were reported in chapter II.

Compound III-1: 1,8-Naphthalic anhydride (1.50 g, 7.57 mmol) and n-hexylamine (3.0 mL) were placed in a 10 mL round-bottomed flask. The mixture was heated at reflux for 5 h. The reaction was cooled and poured into an aqueous HCl solution (20 mL of water and 4 mL of concentrated HCl). The resulting solid was filtered and washed with water until free from acid. After recrystallization from methanol and drying in a

vacuum oven at 50 °C, compound III-1 was obtained: 2.02 g (95%); m.p. 75-77 °C; IR (KBr) 1702, 1664 cm^{-1} (imide); HRMS for $\text{C}_{18}\text{H}_{19}\text{NO}_2$, calcd. 281.1416, found 281.1400 (Int, 74.1%); ^1H NMR (200 MHz, CDCl_3) 8.47-8.43 (d, 2 H, $J = 7.18$ Hz), 8.09-8.05 (d, 2 H, $J = 8.28$ Hz), 7.66-7.58 (m, 2 H), 4.12-4.03 (t, 2 H, $J = 7.55$ Hz), 1.66 (m, 2 H), 1.29 (m, 6 H), 0.82 (m, 3 H); ^{13}C NMR (50 MHz, CDCl_3) 164.17, 134.13, 131.45, 127.26, 123.09, 40.89, 32.01, 28.51, 27.27, 23.03, 14.53.

III.6.References

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Chapter IV

Polyimides Derived from Unsymmetric Dianhydride

IV.1. Introduction

Much effort has been directed toward the design and synthesis of new dianhydride and diamine monomers for making the polyimides with desirable properties and functions. There are mainly two structural variations for aromatic dianhydride monomers: 5-membered phthalic and 6-membered naphthalic dianhydrides (Figure IV.1).

Figure IV.1. Structures of 5-membered and 6-membered aromatic dianhydrides

As proposed in chapter I, replacing one of phthalic anhydrides in BTDA with a naphthalic anhydride would give a new unsymmetric dianhydride IV-4 (Scheme IV.1) which to our knowledge has not been reported in the literature. Since the new monomer is molecularly unsymmetric, the resulting polyimides should possess a better solubility than the BTDA- and bis(naphthalic anhydride)-based polyimides⁶ and maintain other desirable properties such as high thermal stability (due to the naphthalimide unit). The synthesis and polymerization of unsymmetric dianhydride IV-4 was reported in this chapter.

IV.2. Monomer synthesis and characterization

IV.2.1. Monomer synthesis

The unsymmetric dianhydride IV-4 can be synthesized by the Friedel-Crafts reaction of 3,4-dimethylbenzoyl chloride with acenaphthene or by the reaction of trimellitic anhydride chloride derivative with acenaphthene (Scheme IV.1).

Scheme IV.1. Retrosynthetic analysis for the unsymmetric dianhydride.

The Friedel-Crafts reaction between acenaphthene and trimellitic imide chloride was attempted first in the presence of AlCl_3 in nitrobenzene. It was possible to make the target product, but it was difficult to purify the product due to the isomers, as detected by TLC. Thus a second route was pursued.

1-Benzoylnaphthalene-3',4,4',5-tetracarboxylic dianhydride (BNTDA, IV-4) was readily synthesized in four steps from acenaphthene and 3,4-dimethylbenzoyl chloride (Scheme IV.2).

Scheme IV 2. Synthesis of unsymmetric dianhydride (BNTDA).

The acylation reaction of acenaphthene with 3,4-dimethylbenzoyl chloride using AlCl_3 as catalyst in CH_2Cl_2 produced compound IV-1 in 93% yield. Oxidation of compound IV-1 with an excess of sodium dichromate in acetic acid gave compound IV-2 in 84% yield. The following oxidation of compound IV-2 with potassium permanganate was conducted, but the yield was low and the resulted product was difficult to be purified. Another oxidation of compound IV-2 was performed with oxygen in the presence of cobalt acetate in acetic acid and afforded compound IV-3 in 68% yield. In the above three reactions, the product of each reaction was pure enough for the subsequent reaction. Dehydration of compound IV-3 with acetic anhydride gave dianhydride IV-4. The pure monomer was obtained by recrystallization from 1,2-dichlorobenzene or by sublimation under vacuum.

IV.2.2. Characterization

The structure of unsymmetric dianhydride (BNTDA) was unambiguously confirmed by IR, ^1H and ^{13}C NMR spectroscopies and high-resolution mass spectrometry. In their IR spectra, the dianhydride monomer showed characteristic anhydride peaks at 1856, 1779, 1737 cm^{-1} and ketone peak at 1672 cm^{-1} . The ^1H and ^{13}C NMR were also consistent with the assigned structures of unsymmetric dianhydride.

Figure IV.2. IR spectrum of unsymmetric dianhydride.(BNTDA).

The assignment of ^1H NMR spectrum of monomer BNTDA was possible in conjunction with the COSY experiment and is shown in Figure IV.3. The proton labeled H_1 appears as a doublet at 8.60 ppm with a coupling constant of 7.52 Hz with neighboring proton H_2 . The proton labeled H_3 appears as a doublet of doublets at 8.38 ppm with coupling constants of 8.52 and 0.96 Hz with neighboring H_7 and H_6 . The proton labeled H_5 appears as a doublet of doublets at 7.98 ppm with coupling constants of

8.00 and 1.80 Hz with neighboring H₄ and H₃. The proton labeled H₇ appears as a doublet of doublets at 7.92 ppm with coupling constants of 8.52 and 1.16 Hz with neighboring H₈ and H₆.

In the ¹³C NMR spectrum (Figure IV.4), there is one peak at 194.50 ppm for the ketone and four peaks at 168.37-160.26 ppm for the anhydride carbonyl groups. The remaining peaks are difficult to identify specifically but add up to the appropriate number of quaternary and methine carbons. The results from high resolution mass spectra further confirmed the structure of the unsymmetric dianhydride.

Figure IV.3. ¹H NMR spectra of unsymmetric dianhydride IV-4.

Figure IV.4. ^{13}C NMR spectra of unsymmetric dianhydride IV-4.

IV.3. Polymer synthesis and characterization

IV.3.1. Model compound

IV.3.1.1. Model reactions

Unlike the commercially available aromatic dianhydride, the BNTDA monomer contains two different anhydrides, i.e. naphthalic and phthalic anhydrides, and it was reported that naphthalic anhydride does not react with aromatic amines under 140 °C.⁷ In order to further investigate the reactivity of anhydride groups in BNTDA monomer, the model reaction of monomer IV-4 with 3,5-di-*tert*-butylaniline was first carried out in DMAc in the presence of pyridine at room temperature (Scheme IV.3). After 3 h, additional pyridine and acetic anhydride were added and the temperature rose to 60 °C. After another 3 h, the reaction was stopped and anhydride-imide IV-5a was isolated in 92% yield. When the same reaction was carried out for 4 h in *m*-cresol at 200 °C, anhydride-imide IV-5a was found to be formed faster than diimide IV-5b and the latter was eventually isolated in 96% yield. The melting points of compounds IV-5a and IV-5b were 306.1 and 169.4 °C, respectively.

Scheme IV.3. Model reactions of dianhydride IV-4 and 3,5-di-*tert*-butylaniline.

IV.3.1.2. Characterization of model compounds

The structures of model compounds IV-5a and IV-5b were confirmed by IR, ¹H and ¹³C NMR spectroscopies and mass spectrometry. Figure IV.5 shows the IR spectra of BNTDA monomer, model compound IV-5a and 5b. Comparing with the IR spectrum of BNTDA, model compound IV-5a shows two peaks at 1774 and 1742 cm⁻¹ for the naphthalic anhydride, and two peaks at 1782 and 1722 cm⁻¹ corresponding to the phthalimide group. Model compound IV-5b shows three carbonyl peaks at 1781, 1723, and 1673 cm⁻¹ due to the naphthalimide, phthalimide and ketone groups.

Figure IV.5. IR spectra of BNTDA monomer, model compounds IV-5a and 5b.

The ¹H NMR spectrum of compound IV-5a displays a distinct peak at δ 1.37 ppm for the methyl groups; while two peaks at δ 1.40 and 1.37 ppm are shown for two sets of magnetically non-equivalent methyl groups in compound IV-5b. The ¹³C NMR spectra are also consistent with the structures of compounds IV-5a and IV-5b. The model reactions demonstrated that reactivity of the 5-membered ring anhydride is different from the 6-membered ring anhydride and the former is more reactive than the latter. At room temperature, only the phthalic anhydride unit in BNTDA monomer reacts towards an aromatic amine and the naphthalic anhydride is inert. At high temperature (200 °C), both anhydrides are reactive to aromatic amines.

IV.3.2. Polymerization

On the basis of the results from the model reactions, one-step polymerizations of dianhydride IV-4 with various aromatic diamines IV-7a-d (Scheme IV.4) were then carried out in *m*-cresol in the presence of a small amount of isoquinoline at 200 °C. 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 6% to 12% (wt/v). With rigid and or linear diamines (e.g., *p*-phenylenediamine and ODA), the solution concentration was kept low in order to prevent gel formation. For flexible or less linear diamines, the solution concentration should be maintained as high as possible to suppress the formation of cyclic oligomers. High molecular weight polyimides IV-6b-d were readily formed in 16 h, except for polyimide IV-6a, which precipitated out during polymerization.

Scheme IV.4. Synthesis of polyimides (IV-6a-d).

IV.3.3. Characterizations

The structures of these polyimides were characterized by IR spectra. The IR spectrum of monomer IV-4 shows three peaks at 1856, 1779 and 1737 cm^{-1} for the naphthalic and phthalic anhydrides; while the IR spectra of these polyimides display three imide peaks at 1781, 1724 and 1673 cm^{-1} similar to that of diimide IV-5b. Polyimides IV-6b-d were found to be soluble in *m*-cresol, N-methylpyrrolidinone (NMP) and 1,1,2,2-

tetrachloroethane (TCE) at ambient temperatures (Table IV.1). Some were even soluble in chloroform and N,N-dimethylacetamide (DMAc). Compared with polyimide IV-8 derived from BTDA and (ODA), polyimides derived from BNTDA are significantly more soluble in organic solvents. Apparently, such an improvement in solubility can be attributed to the unsymmetric structure of BNTDA and the resulting three possible diad microstructures within the polyimide backbone. Polyimides IV-6b-d had an inherent viscosity ranging from 0.44 to 0.73 dL/g in NMP at 30 °C (Table IV.1).

Table IV.1. Characterizations of polyimides IV-6a-d, and IV-8.

Polymer	η_{inh}^a dL/g	Solubility ^b			
		NMP	DMAc	TCE	CHCl ₃
IV-6a	N/M	-	-	-	-
IV-6b	0.73	+	-	+	±
IV-6c	0.56	+	-	+	±
IV-6d	0.44	+	+	+	+
IV-8 ^c	N/M	-	-	-	-

^a Inherent viscosity measured in NMP at 30 °C; N/M: Not measured due to low solubility in organic solvents listed in the table. ^b Measured at room temperature; Key: +, soluble; ±, partially soluble; -, insoluble. ^c Made from BTDA and ODA.

IV.3.4. Polymer properties

IV.3.4.1. Thermal and mechanical properties

Glass Transition Temperatures (T_g)

The glass transition temperatures (T_g) of polyimides IV-6a-d were measured by differential scanning calorimetry (DSC). The T_g of polyimides IV-6b, 6c and 6d were 360, 285 and 370 °C, respectively, and the T_g of polyimide IV-6a was not detectable by

DSC. (Table IV.2) In comparison with the T_g (293 °C) of polyimide IV-8, the T_g value of BNTDA-based analogue IV-6b increased by 67 °C. Evidently, the increase in T_g is attributable to the fused and rigid naphthalimide unit in the polymer.

Table IV.2. Thermal properties of polyimides IV-6a-d, and IV-8.

Polymer	T_g^a (°C)	T_d^b (°C)
IV-6a	N/O	476
IV-6b	360	478
IV-6c	285	500
IV-6d	370 ^c	522
IV-8 ^d	293	544

^a Obtained from the second DSC scan at a heating rate of 10 °C/min in nitrogen; N/O: Not observed. ^b 5% weight loss at a heating rate of 10 °C/min in nitrogen. ^c Obtained from the first scan of ODSC at a heating rate of 3 °C/min in nitrogen. ^d Made from BTDA and ODA.

Decomposition Temperatures

The decomposition temperatures (T_d), as assessed by the onset temperature of 5% weight loss by TGA, occurred in the range of 476-522 °C in nitrogen for polyimides IV-6a-d (Table IV.2). In comparison with the T_d (544 °C) of polyimide IV-8, the T_g value of BNTDA-based analogue IV-6b decreased by 66 °C.

Young's Moduli

Thin rectangular strips of polymer films cast from *m*-cresol solution were used to measure Young's modulus using TMA in the tensile stress-strain mode. Loads were chosen such that a linear stress-strain relationship was obtained. At 25 °C, the Young's moduli (E') were 1.66 and 1.54 GPa for polyimides IV-6b and IV-6c, respectively. In comparison, these polyimides appear to have lower tensile moduli than BTDA based

polyimides (2.0 GPa). The low tensile moduli may be due to the unsymmetric structure of the polyimides. However, it should be noted that different casting and TMA experiment conditions can vary the TMA data. The film of polyimide IV-6d was not tough enough for TMA measurement. At 200 °C the Young's moduli for polyimides IV-6b and IV-6c decreased to 1.24 and 0.98 GPa. One of the typical TMA diagram of polyimide IV-6b was shown in Figure IV.6. A loss of modulus could clearly be seen in the E' curve and the T_g value taken as a maximum of $\tan \delta$ in the TMA experiment was lower than the one obtained by DSC.

polyimide IV-6b

Figure IV.6. TMA diagram of polyimide IV-6b.

IV.3.4.2. Electrochemical and electrochromic properties

Electrochemical properties.

The cyclic voltammogram of polymer IV-6d was obtained in DMF containing 0.1 M n-Bu₄NClO₄ (Figure IV.7). The polyimide IV-6d presents three reversible and stable redox couples ($E_{pc1} = -1.08$ V, $E_{pc2} = -1.47$ V, $E_{pc3} = -1.76$ V, $E_{pca1} = -0.74$ V, $E_{pca2} = -0.98$ V, $E_{pca3} = -1.45$ V), which are similar to that reported for the BTDA based model imide compounds and polymers.

Polyimide IV-6d

Figure IV.7. Cyclic voltammogram of polyimide IV-6d at platinum electrode in DMF.

Electrolyte: 0.1 M n-Bu₄NClO₄. Scan rate: 100 mV/s.

Viehbeck *et al.* reported the potential for the first electron reduction E_{pc1} shifts to more positive values for the imide compounds in the following order: phthalimide < naphthalimide < BPDA < BTDA < PMDA < NTDA < PTDA and the changes in the aromatic imide structures have much greater effect on the reduction potentials than that of the N-substituents (Figure IV.8). So, one possible redox mechanism involving three one-electron transfer reactions is given in Scheme IV.5. The first electron reduction at -1.08 V gives the radical-anion form. However, the second reduction at -1.47 V probably leads to a diradical-dianion state. This representation gives the largest degree of electron separation by the BNTDA ketone group. The BNTDA moiety allows a third electron reduction to the radical-trianion form as depicted in Scheme IV.6. The third electron transfer occurs a few hundred millivolts more negative than the redox potential for the second reduction (-1.76 V).

Figure IV.8. Structure of imide systems.

Scheme IV.5. Proposed redox reactions for BNTDA-based polyimides.

Electrochromic properties.

The electrochromic properties of polyimides derived from BNTDA were studied by applying a range of negative potentials on the polyimide coated ITO glass electrode. In correlation with the redox processes, the polymer films displayed reversible color changes. Figure IV.9 shows the in-situ UV-visible spectra of a polyimide IV-6d film which was dipped in a 0.1 M TBAPC- DMF solution at different applied potentials. At 0.0 V, the polymer film is nearly colorless with a maximum absorption at 338 nm. When the applied potential decreased to -1.2 V, the intensity of this band decreased and the polymer film turned blue with the appearance new peaks at 441 and 564 nm. Along with further decrease of the potential, the intensities of these absorption bands continued to increase and the color of the polymer film become dark blue.

Figure IV.9. In-situ UV-Visible spectra of polyimide IV-6d film in 0.1 M TBAPC-DMF solution at 0.0, -1.2 , -1.5 , -1.8 , and -2.1 V.

IV.3.4.3. Optical properties of polyimides

Refractive indices

The refractive indices of the polyimides IV-6b-d at different wavelength were determined by the spectroscopic ellipsometry on a thin film (~200 nm) on silicon substrates.⁸ Polyimide IV-6a was difficult to cast films due to its poor solubility. One of ellipsometric spectra of polyimide IV-6b film with a thickness of 215 nm and MSE of 7.492 was shown in Figure IV.10. The refractive indices of polymer IV-6b-6d are in the range of 1.6639-1.7085, 1.6658-1.7104 and 1.6754-1.7200 at 1.55, 1.31 and 0.85 μm , respectively (Table IV.3). Refractive index is related to the ratio of the induced dipole moment to the molar volume and is known to decrease as the polarizability of chemical bonds decreases.⁹ Relative to the structural changes in the diamine component, the refractive indices decrease in the order of IV-6b > IV-6c > IV-6d for the BNTDA based polyimides.

Table IV.3. Refractive indices of polyimides IV-6a-d at different wavelength.

Polyimides	1.55 (μm)	1.31 (μm)	1.2 (μm)	1.0 (μm)	0.85 (μm)
IV-6b	1.7085	1.7104	1.7116	1.7152	1.7200
IV-6c	1.6856	1.6868	1.6877	1.6907	1.6954
IV-6d	1.6639	1.6658	1.6670	1.6706	1.6754

Figure IV.10. Generated and experimental ellipsometric spectra of polyimide IV-6d.

Dependence of refractive indices on wavelength

The dependence of refractive indices on wavelength in polyimide films IV-6b-6d on silicon substrate is shown in Figure IV.11. The refractive indices of the polyimides decrease monotonically with increasing wavelength. The phenomena agree with the results reported by Matsuura et al on the TFDB based polyimides.¹⁰

Figure IV.11. Dependence of refractive indices of polyimides IV 6b-d on wavelength.

IV.4. Conclusions

New unsymmetric dianhydride BNTDA was successfully synthesized from acenaphthene and 3,4-dimethylbenzoyl chloride. The polyimides derived from the novel dianhydride displayed improved solubility and thermal stability, and also showed electroactive and electrochromic properties. Moreover, the anhydride groups in BNTDA monomer showed different reactivity towards aromatic amines.

IV.5.Experimental section

Materials

Acenaphthene, 3,4-dimethylbenzoic acid, *m*-cresol, isoquinoline, thionyl chloride, dichloromethane, anhydrous aluminum chloride, sodium dichromate dihydrate, cobalt acetate tetrahydrate, bromoacetic acid, acetic anhydride, and 1,2-dichlorobenzene were purchased from Aldrich Chemical Co and used without further purification. *p*-Phenylenediamine (IV-7a) (Aldrich) was purified by sublimation under vacuum. 4,4'-Oxydianiline (IV-7b) (Aldrich) was recrystallized from ethanol. 4,4'-(1,3-Phenylenedioxy)dianiline (IV-7c), and 4,4'-fluorenedianiline (IV-7d) were received from New Seika Corp. and used without further purification. Supporting electrolyte tetra-*n*-butylammonium perchlorate (Bu_4NClO_4) was purchased from Fluka. *N,N'*-Dimethylacetamide (DMAc) was vacuum distilled from CaH_2 . Other common organic solvents are reagent grade unless otherwise stated. Indium tin oxide (ITO) coated glass was purchased from Delta Technologies Ltd.

Measurements

The ^1H and ^{13}C NMR spectra were recorded on either a Varian Gemini-200 or a Bruker-400 instrument using tetramethylsilane as an internal reference. Infrared measurements were performed on a Bomen Michelson 120 FTIR spectrometer. Low-resolution mass EI and FAB spectra were obtained on VG7070E and Kratos Concept 2H spectrometers, respectively. Melting points were taken from a Fisher-Johns melting apparatus or from a Seiko 220C differential scanning calorimeter (DSC) at a heating rate

of 10 °C/min in nitrogen (100 mL/min). The apparent molecular weights of the polymers were determined by gel permeation chromatography (GPC) relative to polystyrene standards using chloroform at ambient temperature at a flow rate of 1.0 mL/min; an UV detector was set at 254 nm. Inherent viscosities were measured at a concentration of 0.5 g/dL in NMP at 25 °C using an Ubbelohde dilution viscometer. The glass transition temperatures were determined on a Seiko 200 °C DSC at a heating rate of 10 °C/min in nitrogen (100 mL/min). In all cases, the midpoint of change in the slope of the base line from second scan was taken as the T_g. Thermal stabilities, as measured by weight loss, of the polymer samples were determined using a Seiko 120TG /DTA analyzer from 25 to 600 °C at a heating rate of 10 °C/min in nitrogen (200 mL/min).

Film Casting

Polymer films were cast from *m*-cresol solution. A typical procedure is as follows: the purified and dried polymer (100-150 mg) was dissolved in 3-5 mL of *m*-cresol on heating. The solution was then transferred by pipette filtration into a cylindrical glass mold (diameter = 4.0 cm, height = 2.5 cm, thickness = 0.4 cm) placed on a glass plate. The mold was covered with a glass plate. An orifice at the top edge of the mold allowed the solvent to evaporate slowly in a forced-air oven at 130 °C for 36 h to yield tough and flexible films (thickness = 0.05-0.13 mm). The film was removed from the glass mold by adding water to peel off the film. The circular and clear film was then placed in a vacuum oven. The oven temperature was initially at 80 °C for 24 h, then gradually raised to 200 °C, and held at this temperature for 48 h.

Measurement of Mechanical Properties

A typical procedure to obtain tensile mechanical properties of polymers was performed as follows: A stamp was used to cut out a film strip (length = 10 mm, width = 2mm, thickness = 0.025-0.125 mm) which was mounted between two chucks in a 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 = 20-30 g, load amplitude = 5-10 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 t to 450 °C at a ramp rate of 3 °C/min in a static air.

Preparation of Polymer-coated Electrodes

A solution of polymer IV-6c in TCE (25.0 mg/mL) was drop cast or spin coated onto a platinum disc electrode or ITO glass electrode and then dried in an oven at 80 °C for 10 min.

Measurement of Electrochemical and Spectroelectrochemical Properties

Electrochemical measurements were performed using a BAS 100B/W electrochemical workstation interfaced and monitored with a PC computer. The three-electrode system was employed throughout this work, which consists of a working electrode, a silver wire reference electrode and a platinum wire auxiliary electrode. The platinum disc electrode ($s = 0.018 \text{ cm}^2$) for cyclic voltammetry and ITO coated glass

electrode ($0.5 \times 2.5 \text{ cm}^2$) for UV-Vis spectrophotometry were used, respectively. In all cases, the electrolyte solutions were deoxygenated with nitrogen for 10 min prior to use.

Spectroelectrochemical measurements were carried out by combining an electrochemical workstation with a Perkin-Elmer Lambda 900 Spectrophotometer and using a quartz cuvette cell containing an ITO working electrode, a platinum wire auxiliary electrode and a silver wire reference electrode. A blank ITO glass electrode with the electrolyte solution was used as reference.

Measurement of Optical Properties

A typical procedure to prepare polymer film for optical measurement is as follows: A solution of polymer IV-6c in TCE (25.0 mg/mL) was spin coated onto a silicon wafer, then dried in an oven at 100 °C for 3h. To determine optical constants of polymer films, Variable Angle Spectroscopic Ellipsometry was performed with a J. A. Woollam Co. Variable Angle Spectroscopic Ellipsometer (VASE) equipped with PTI monochromator and 4 nm bandwidth. A polymer film with thickness of about 200 nm was fit for thickness and optical constants simultaneously between wavelength of 300 nm and 1800 nm at 10 nm intervals at 65 °, 70 ° and 75 ° incident angles. Simultaneous optical constant and film thickness fitting were done with a Cauchy Model.

Monomer Synthesis.**3,4-Dimethylbenzoyl chloride**

In a 100 mL, round-bottomed flask equipped with a condenser and a drying tube were placed 10.0 g (66.58 mmol) of 3,4-dimethylbenzoic acid and 15 mL (205.97 mmol) of SOCl₂. The mixture was heated to reflux overnight, then distilled the SOCl₂ at atmosphere. The remaining solution was distilled under vacuum (200 mmHg) at 56 °C to give 3,4-dimethylbenzoyl chloride: 10.33 g (92%); ¹H NMR (200 MHz, CDCl₃) δ 7.86 (2 H, s), 7.23 (1 H, s), 2.33 (6 H, s); ¹³C NMR (50 MHz, CDCl₃) δ 167.84, 146.08, 138.06, 132.80, 131.30, 130.72, 129.84, 20.70, 20.18.

5-(3,4-dimethylbenzoyl)acenaphthene (IV-1)

In a flask equipped with a condenser, a nitrogen gas inlet and a stirrer, acenaphthene (2.50 g, 16.21 mmol), 3,4-dimethylbenzoyl chloride (2.73 g, 16.21 mmol) and dichloromethane (20 mL) were placed. Anhydrous aluminium chloride (2.38 g,

17.83 mmol) was then added slowly to the stirred solution while maintaining a temperature of 0 °C. After complete addition, the reaction temperature was allowed to gradually increase to room temperature. The reaction mixture was poured onto crushed ice. The organic layer was partitioned, washed with water, and dried over anhydrous magnesium sulfate. On removal of the solvent, compound IV-1 was obtained as a white solid, which could be recrystallized from acetonitrile: 4.32 g (93%); M.p. 122-123 °C; HRMS for C₂₁H₁₈O, Cald. 286.1363, found 286.1358; IR (KBr) 2918 (C-H), 1646 cm⁻¹ (C=O); ¹H NMR (400 MHz, CDCl₃) δ 7.97 (d, 1 H, J = 8.44 Hz), 7.58 (d, 2 H), 7.45 (m, 2 H), 7.29-7.12 (m, 3 H), 2.26 (s, 1 H), 2.23 (s, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ 197.45, 150.92, 146.09, 142.06, 139.54, 136.93, 136.71, 132.11, 131.42, 131.27, 129.90, 129.47, 129.43, 128.24, 121.56, 120.11, 117.87, 30.49, 30.39, 20.06, 19.77.

4-(3,4-Dimethylbenzoyl)-1,8-naphthalic anhydride (IV-2)

Compound IV-1 (1.00 g, 3.49 mmol) was treated with Na₂Cr₂O₇·2H₂O (4.16 g, 14.0 mmol) in acetic acid (10 mL) for 4 h at 100 °C and then poured into water (50 mL). The precipitate was filtered, washed with water and acetic acid and dried at 100 °C in an oven overnight. The product was purified by recrystallization from acetic acid to give compound IV-2: 0.97 g (84%); IR (KBr) 1773, 1738 (naphthalic anhydride), 1656 cm⁻¹ (C=O); ¹H NMR (200 MHz, CDCl₃/CF₃COOD) 8.69-8.64 (m, 2 H), 8.41-8.36 (d, 1 H),

7.85-7.80 (m, 2 H), 7.63 (s, 1 H), 7.53-7.49 (d, 1 H), 7.25-7.21 (d, 1 H); ^{13}C NMR (50 MHz, $\text{CDCl}_3/\text{CF}_3\text{COOD}$) δ 199.1, 161.8, 161.5, 147.0, 144.1, 138.4, 135.1, 134.3, 133.9, 133.2, 132.5, 132.1, 130.8, 129.6, 129.4, 129.1, 127.9, 120.1, 118.5, 20.5, 19.8.

Unsymmetric dianhydride (IV-4)

In a three-necked flask equipped with a condenser, a gas inlet and a stirrer, compound IV-2 (0.50 g) was dissolved in 15 mL of refluxing acetic acid (120 °C). Cobalt acetate tetrahydrate (0.37 g) and bromoacetic acid (0.21 g) were then added. The oxygen was then bubbled into the reaction solution for 8 h. After the reaction solution was cooled to room temperature, it was poured into water (50 mL). The precipitate was collected by filtration, washed with water and dried in an oven at 100 °C (0.40 g, 68% yield). The crude acid IV-3 was dissolved in 8 mL of acetic anhydride and heated to reflux. When the solution became clear, it was cooled to room temperature. The monomer IV-4 was filtered, washed with dry toluene and dried in an oven 100 °C, which was further purified by recrystallization from 1,2-dichlorobenzene or by sublimation: 0.33 g (85% yield); M.p. 272 °C (DSC); IR 1856, 1779, 1737 (naphthalic and phthalic anhydrides), 1672 cm^{-1} (ketone); HRMS for $\text{C}_{21}\text{H}_8\text{O}_7$, Cald. 372.0270, found 372.0261;

^1H NMR (400 MHz, DMSO- d_6) δ 8.61-8.57 (m, 2 H), 8.40-8.38 (dd, 1 H, $J = 8.52, 0.96$ Hz), 8.05-7.90 (m, 4 H), 7.82-7.80 (d, 1 H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 190.50, 168.37, 167.24, 160.47, 160.26, 141.15, 138.58, 137.66, 132.77, 132.65, 132.48, 132.14, 131.17, 130.14, 128.92, 128.79, 128.60, 128.17, 121.69, 119.80.

Model compound (IV-5a)

In a flame-dried 25 mL, three neck, round-bottomed flask equipped with a nitrogen inlet/outlet and a magnetic stirrer, were added dianhydride IV-4 (0.5000 g, 1.343 mmol), 3,5-di-*tert*-butylaniline (0.2758 g, 1.343 mmol), 6 mL of DMAC and 10 drops of pyridine. The solution was stirred at room temperature under nitrogen for 4 h, then an additional 10 drops of pyridine and 10 drops of acetic anhydride were added. The solution was heated at 60-70 °C for another 3h and poured into 50 mL of methanol. The model compound was collected by filtration and washed with methanol. After drying at 100 °C in an oven for 20h, model compound IV-5a was obtained: 0.69 g (92 %); m.p. 306.1 °C (DSC); IR 1782, 1774, 1742, and 1722 cm^{-1} ; MS (Fab) for $\text{C}_{35}\text{H}_{29}\text{NO}_6$: Cald, 560; found, 1120 (dimer) (1%); ^1H NMR (400 MHz, $\text{CDCl}_3/\text{CF}_3\text{COOD}$) δ 8.78-8.76 (dd, 2 H, $J = 7.28$ Hz), 8.77-8.75 (d, 1 H, $J = 7.44$ Hz), 8.53-8.51 (dd, 1 H, $J = 8.56, 0.96$ Hz), 8.39-8.37, (dd, 1 H, $J = 7.76, 1.44$ Hz), 8.34 (s, 1 H), 8.17-8.15 (d, 1 H, $J = 7.72$ Hz),

7.95-7.91 (dd, 1 H, $J = 8.56, 7.36$ Hz), 7.94-7.92, (d, 1 H, $J = 7.44$ Hz), 7.53-7.52, (t, 1 H, $J = 1.68$), 7.20, (s, 1 H), 7.20 (s, 1 H), 1.37 (s, 18 H); ^{13}C NMR (100 MHz, $\text{CDCl}_3/\text{CF}_3\text{COOD}$) δ 194.00, 166.65, 166.62, 160.03, 159.83, 152.14, 141.93, 141.46, 136.19, 135.91 134.35, 132.98, 132.45, 132.08, 130.74, 130.23, 129.48, 129.09, 128.18, 125.25, 124.45, 123.15, 121.40, 120.98, 119.17, 35.04, 31.31.

Model compound (IV-5b)

To a flame-dried 50 mL, three neck, round-bottomed flask equipped with a nitrogen inlet/outlet and a magnetic stirrer were added dianhydride IV-4 (0.5000 g, 1.343 mmol), 3,5-di-*tert*-butylaniline (0.5516 g, 2.686 mmol), *m*-cresol (10 mL) and isoquinoline (5 drops). The reaction mixture was heated up to 200 °C for 4 h under nitrogen, then precipitated into methanol. After filtration and washed with methanol, model compound IV-5b was dried in an oven under vacuum at 100 °C overnight. The yield was 0.96 g (96%); m.p. = 169.4 °C (by DSC); IR, 1781, 1723, and 1673 cm^{-1} ; MS (Fab) for $\text{C}_{49}\text{H}_{50}\text{N}_2\text{O}_5$, calcd. 747, found, 747 (67%); ^1H NMR (400 MHz, CDCl_3) δ 8.78-8.74 (m, 2 H), 8.47-8.45 (dd, 1 H, $J = 8.52, 0.88$ Hz), 8.39-8.37 (dd, 1 H, $J = 7.72, 1.40$ Hz), 8.33 (s, 1 H), 8.15-8.13 (d, 1 H, $J = 7.72$ Hz), 7.90-7.86 (m, 2 H), 7.58-7.57 (t, 1 H, $J = 1.68$ Hz), 7.52-7.51 (t, 1 H, $J = 1.68$ Hz), 7.28-7.17 (m, 4 H), 1.40 (s, 18 H), 1.37 (s, 18

H); ^{13}C NMR (50 MHz, CDCl_3) δ 194.91, 166.61, 166.45, 164.26, 163.87, 152.20, 152.14, 142.66, 140.44, 136.24, 136.04, 134.56, 132.73, 132.55, 131.78, 130.79, 130.23, 129.62, 129.29, 128.85, 128.23, 126.04, 125.45, 124.45, 123.76, 123.34, 123.16, 122.79, 121.26, 35.28, 31.72, 31.63.

Polymerization

All of the polyimides were prepared by the reaction of dianhydride IV-4 with aromatic diamines in the presence of isoquinoline in *m*-cresol at 200 °C. A typical procedure for the preparation of polyimide IV-6b is as follows: To a flame-dried 50 mL, three neck, round-bottomed flask were added dianhydride IV-4 (1.000 g, 2.686 mmol), diamine 7b (0.5378 g, 2.686 mmol), *m*-cresol (30 mL) and isoquinoline (5 drops). The reaction mixture was heated up to 200 °C under nitrogen and held at this temperature for 16 h. During the course of reaction, about 10 mL of *m*-cresol was distilled off. The reaction was cooled to about 100 °C. The polymer was precipitated into methanol (200 mL) and collected by filtration. The polymer was further washed with acetone using a Soxhlet extractor overnight. After drying under vacuum at 150 °C, polyimide IV-6b was obtained as a powder: 1.31 g (91%).

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Chapter V

Copolyimides Derived from Unsymmetric Dianhydride

V.1. Introduction

Block copolyimides have been paid much attention since they afford improved solubility, processability and other desired properties than homopolyimides. For example, block copoly(imide dimethylsiloxane)s have good processability and adhesion, and low water absorption and dielectric constants;¹ block copolyimides have better solubility than homopolyimides;² block copoly(urethane-imide)s show good solubility and elasticity.³ Usually, the block or segmented copolymer can be made through a poly(amic acid) precursor by combining a dianhydride monomer or anhydride-terminated imide oligomer with other amine or isocyanate-terminated prepolymer.⁴

Due to the two kinds of different anhydride functional groups in BNTDA (Chapter 4), the dianhydride monomer has different reactivity under different reaction conditions. At low temperatures, only phthalic anhydride is reactive towards aromatic amine; at high temperatures, both anhydrides (phthalic and naphthalic) are reactive. Based on this specific property, BNTDA can be used as an end-capping agent to prepare imide oligomers. These oligomers will be stable at low temperatures, inert towards moisture and they can perform a reaction with different amine or isocyanate-terminated prepolymers at high temperatures leading to perfectly alternating block copolymers.

In this chapter, we present a new approach to preparing oligomers end-capped with reactive naphthalic anhydride group and the synthesis block copolymers based on

these oligomers. In addition, the effect of different monomer-adding sequence on the thermal properties of copolyimides was also probed.

V.2. Oligomer synthesis and characterization

V.2.1. Model compound

Synthesis

As mentioned in chapter 4, naphthalic and phthalic anhydride groups present in BNTDA monomer have different reactivity under certain reaction conditions. At ambient temperatures, phthalic anhydride is reactive towards aromatic diamines, but naphthalic anhydride is inert. At high temperatures such as 200 °C, both anhydride groups are reactive and phthalic anhydride reacts faster than the naphthalic anhydride. In this study, ODPA and BAPP were used to obtain soluble polyimide oligomers and BNTDA was used as the end-capping agent. In order to further investigate the anhydride reactivity presented in BNTDA towards aromatic diamine BAPP, a model reaction of BNTDA with BAPP was carried out in DMAc in the presence of pyridine at room temperature. The solution was allowed to stir for 12 h and then additional pyridine and acetic anhydride were added to the reaction flask and the solution was heated to 60 °C. After another 12 h, model naphthalic dianhydride V-1 containing phthalimide was prepared in quantitative yield (Scheme V.1). Compound V-1 can also be used as a dianhydride monomer to make an alternating copolyimide with another aromatic diamine.

Scheme V.1. Model reaction of dianhydride BNTDA and diamine BAPP.

Characterization

The structure of model compound V-1 was characterized by IR, ¹H NMR and ¹³C NMR. The infrared spectrum (Figure V.1) of the model dianhydride V-1 shows naphthalic anhydride and phthalimide C=O stretching at 1782, 1744 and 1721 cm⁻¹ with the C=O stretching at 1667 cm⁻¹. The ¹H NMR spectrum of the model dianhydride V-1 displays a distinct peak at δ 1.64 ppm for the methyl groups and four double peaks at δ 7.43-6.98 ppm for the aromatic protons from diamine. The peaks at δ 8.64-7.91 ppm are from protons of BNTDA. The ¹³C NMR spectrum is also consistent with the structure of the model dianhydride. The model reaction study of BNTDA and BAPP clearly demonstrates the different reactivity of anhydrides presented in BNTDA towards

aromatic amine and the capability of BNTDA as end capping agent in the synthesis of oligomers.

Figure V.1. IR spectra of model dianhydride V-1.

V 2.2.Preparation of BNTDA end-capped oligomers

Synthesis

The two-step synthesis method is well known in the preparation of oligoimides or polyimides from dianhydrides and diamines. The first step is carried out in aprotic polar solvent to form amic acid and the second one is chemical imidization to form imides. ODPA and BAPP were used as monomer to prepare oligomers. Thus these oligomers would show good solubility in common organic solvent, which was good for the

characterization and performing reaction with other end-capped oligomers. Oligomers V-2a-b were prepared by two-step synthesis, using ODPA and BAPP as monomers and BNTDA as end capping agent. The degree of polymerization was controlled by the balance of two monomers (ODPA and BAPP), according to the equation:⁵

$$\langle X_n \rangle = 2 DP = (1 + r) / (1 + r - 2rp)^* \quad (1)$$

Here, X_n is the number average degree of polymerization, DP is the degree of polymerization and is defined as the average number of repeating units per polymer molecule, r is the stoichiometric imbalance between monomers and p is the fraction of amine groups that have reacted at a given stage of the reaction. If $p \rightarrow 1$,

$$\langle X_n \rangle = 2 DP = (1 + r) / (1 - r)^* \quad (2)$$

The procedure used to make BNTDA terminated imide oligomers is shown in Scheme V.2. Two kinds of oligomers V-2a-b with calculated molecular weight 10710 and 12710 g/mol were synthesized. Since BNTDA is not included in the stoichiometry, the ODPA and BAPP monomers are present in a nonstoichiometric ratio. A stoichiometric excess of the diamine was added to the dianhydride in DMAc with the presence of pyridine. After stirring for 24 h at room temperature, an excess of the BNTDA was added into solution to ensure quantitative endcapping and the solution was stirred at room temperature for 8 h. Then, pyridine and acetic anhydride were added and the reaction temperature was raised to 60 °C. Imidization took place to form a BNTDA-terminated imide oligomer. After stirring the solution for additional 10 h, the oligomer was isolated by precipitating the solution in methanol.

Scheme V.2. Synthesis of oligomers V-2a-b end capped with BNTDA.

Characterization of oligomers

The IR spectra showed that the imide oligomers V-2a-b were fully imidized with characteristic imide peaks appearing at 1779 and 1724 cm^{-1} (Figure V.2-a). Due to the

reduced molar ratio of BNTDA in the oligomer compared to model compound V-1, the peaks at 1774 and 1667 cm^{-1} were difficult to distinguish.

Figure V.2. IR spectra of oligomer V-2a (a) and copolymer V-3a (b).

The molecular weights of oligomers were determined by end group analysis. The oligomers V-2a-b were reacted with 4-bromoaniline to yield bromine end-capped oligomers (Scheme V.3). The molecular weights of oligomer V-2a and 2b obtained from Br analysis were 6860 and 7930 g/mol, respectively, which were lower than the theoretical values calculated from the molar ratios. Since the purification of high molecular weight oligomers is difficult, relatively low precision was expected. Nevertheless, a reasonable estimate of the molecular weight was achieved.

Scheme V.3. Reactions of oligomers V-2a-b with 4-bromoaniline.

Gel permeation chromatography (GPC) and inherent viscosities were also used to determine the molecular weight of BNTDA-terminated oligomer. Intrinsic viscosities of oligomers V-2a-b were 0.10 and 0.25 dL/g in CHCl_3 and the apparent weight-average molecular weight of oligomers V-2a-b measured by GPC relative to polystyrenes were 5100 and 8900 (Table V.1). The molecular weight distribution (PDI) for the oligomers were close to the most probable distribution of 2.0. This was a good indication that only one reaction mechanism operated and that it proceeded to essentially complete conversions.

Table V.1. Characterization of oligomers V-2a-b.

Polymer Code	η_{inh}^a (dL/g)	GPC ^b			DSC ^c Tg (°C)	TGA ^d
		Mw ($\times 10^4$)	Mn ($\times 10^4$)	PDI		
Oligomer V-2a	0.10 ^e	0.51	0.26	1.97	206	446
Oligomer V-2b	0.25	0.89	0.47	1.90	217	505

^a Inherent viscosity measured in CHCl_3 at 25 °C; ^b Determined by GPC relative to polystyrene standards; ^c Obtained from the second DSC scan at a heating rate of 10 °C/min in nitrogen; ^d 5% weight loss at a heating rate of 10 °C/min in nitrogen; ^e measured in CHCl_3 with 5 drops of CF_3COOH .

The other typical properties of imide oligomers were also listed in Table V.1. Generally, low molecular weight oligoimides show a lower glass transition temperature (Tg) than the corresponding high molecular weight homopolyimide. Moreover, the Tg of the oligomers increase along with the DP and tend to the Tg of homopolymer. Here, the Tg and thermal stability of oligomers V-2a-b were measured by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The Tg (217 °C) of oligomer

V-2b was higher than that of oligomer V-2a due to the relatively high molecular weight. The onset temperature of oligomer V-2b for 5% weight loss in N₂ was also higher than that of oligomer V-2a. Both of the oligomers had lower T_g and thermal stability than homopolymer V-4, which has a T_g of 228 °C and onset temperature of 521 °C for 5% weight loss in N₂. It clearly demonstrated that the length or molecular weight of oligomer has important influences on their thermal properties. So, the thermal properties of block copolymers can be tailored through controlling the length or molecular weight of precursor oligomers. As we expected, these imide oligomers made from ODPA and BAPP show good solubility in common organic solvents such as DMAc, DMF, TCE and THF (Table V.2).

Table V.2. Solubility of oligomers V-2a-b.

Polymer Code	Solubility ^a					
	<i>m</i> -cresol	DMAc	DMF	TCE	CHCl ₃	THF
oligomer V-2a	+	+	+	+	+	+
oligomer V-2b	+	+	+	+	-	+

^a Measured at room temperature; Key: +, soluble; -, insoluble.

V.3. Synthesis and characterization of copolymers

V.3.1. Synthesis

IR spectrum was used to determine the difunctionality of the imide oligomers, but it did not show the peaks of naphthalic anhydrides. This was because either the weight percentage of end naphthalic anhydride was too small to measure or the peaks of naphthalic anhydrides overlapped with phthalimide peaks. An additional indirect test of difunctionality is the ability to produce high molecular weight block copolymers when reacted with an appropriate difunctional reagent. A diamine oligomer with molecular weight of 834 g/mol was chosen to accomplish this. The synthesis for the block copolymers is shown in Scheme V.4. Based on the molecular weight of oligomers V-2a-b calculated by element analysis, a certain amount of oligomer was first dissolved in *m*-cresol, then an equimolar quantity of diamine oligomer was added to the solution. The solution was stirred at 200 °C for 4-5 h. After precipitating in methanol, fibrous block copolymers V-3a-b were obtained.

Scheme V.4. Synthesis of block copolyimides V-3a-b.

V.3.2. Characterization

Copolymers V-3a and V-3b had weight average molecular weights of 59700 and 45100, respectively, as measured by GPC (Table V.3), which indicated that highly difunctional monomers were used and the BNTDA terminated imide oligomers prepared by this method were difunctional in nature.

Table V.3. Physical properties of copolymers V-3a-b and homopolymer V-4.

Polymer Code	η_{inh}^a (dL/g)	GPC ^b			DSC ^c T _g (°C)	TGA ^d
		M _w (x 10 ⁴)	M _n (x 10 ⁴)	PDI		
Copolymer V-3a	0.52	5.97	2.19	2.72	-14/203 ^e	441
Copolymer V-3b	0.34	4.51	1.57	2.88	-4/212 ^e	469
Homopolymer V-4	0.59	7.13	4.09	1.74	228	521

^a Inherent viscosity measured in CHCl₃ at 25 °C; ^b Determined by GPC relative to polystyrene standards; ^c Obtained from the second DSC scan at a heating rate of 10 °C/min in nitrogen; ^d 5% weight loss at a heating rate of 10 °C/min in nitrogen; ^e Obtained from the first scan of ODSC at a heating rate of 3 °C/min in nitrogen.

Figure V.3. Gel permeation chromatography traces of (a) oligomer V-2a; (b) the same oligomer after reaction with poly(1,4-butanediol) bis(4-aminobenzoate).

The GPC traces of copolymer V-3a and precursor oligomer V-2a are also shown in Figure V.3. It shows that retention time of copolymer V-3a is much shorter than that of copolymer V-2a, indicating the formation of high molecular weight copolymer. The intrinsic viscosities of the block copolymers are listed in TableV.3. The intrinsic viscosities of both copolymers were relatively high, also indicating that copolymers with high molecular weights were achieved in the copolymerization. The solubilities of these copolymers were tested in common organic solvents. They are soluble in DMAc, DMF, TCE, CHCl₃, etc.. (Table V.4).

Table 4. Solubility of copolymers V-3a-b and homopolymer V-4.

Polymer Code	Solubility ^a					
	<i>m</i> -cresol	DMAc	DMF	TCE	CHCl ₃	THF
copolymer V-3a	+	+	+	+	+	+
copolymer V-3b	+	+	+	+	+	-
homopolymer V-4	+	+	+	+	+	+

^a Measured at room temperature; Key: +, soluble; -, insoluble.

Figure V.4. ODSC traces of (a) copolymer V-3a; (b) copolymer V-3b.

The effects of oligomer size and chemical composition on the T_g and thermal stability of copolymer were assessed by DSC and TGA (Table V.3). It was known that block copolymers made from polyimide and polysiloxane were microphase separation due to the incompatibility. ODSC analysis of the copolymers V-3a-b displayed two transitions corresponding to the lower T_g of the aliphatic chain rich phase and the higher T_g for the polyimide rich phase. (Figure V.4.) Table V.3 listed the T_g values for the copolymers. Both of the copolymers had upper T_g lower than the imide oligomers from which they were made. By comparing the upper T_g of copolymers V-3a-b, it showed that the upper T_g was influenced by the molecular weight of oligoimides. The copolymer

with high molecular weight imide segments has higher upper Tg than copolymer with low molecular weight imide segments. The correlation of Tg with the oligoimide block size in imide siloxane copolymers has also been made by McGrath and co-workers.⁸ The thermal stability of the copolymers as indicated by the values for 5% weight loss in N₂ was determined by TGA (Table V.3). The thermograms of copolymers V-3a-b are shown in Figure V.5. Incorporating the aliphatic oligomers decreased the thermal stability of the copolymers relative to that of the corresponding imide oligomers and homopolyimide. The thermal stabilities of copolymers depend on the size of imide block and copolymers with large imide block size have higher thermal stability than copolymers with small imide block size.

Figure V.5. TGA traces of (a) copolymer V-3a; (b) copolymer V-3b.

V.4. The effect of monomer adding sequences on the properties of copolymers.

V.4.1. Synthesis of copolymers by different monomer adding sequences

The model reaction in chapter IV revealed the difference in reactivity between the two anhydrides in BNTDA monomer under certain reaction conditions. At ambient temperatures, phthalic anhydride is reactive towards an aromatic amine, but naphthalic anhydride is inert. Even at elevated temperatures, the former reacts faster than the latter. Conceivably, under controlled conditions it is possible to obtain structurally ordered copolyimides using BNTDA with two different diamines in one-step polymerization. Thus, three copolymerization experiments were carried out using different sequences for addition of BNTDA, *p*-phenylenediamine (V-4a) and 4,4'-(9-fluorenylidene)dianiline (V-4d) (Scheme V.5). In the first run, all three monomers were added at the beginning, which presumably produced a random copolyimide V-5a. In the second run, diamine V-4a and BNTDA were mixed first and reacted for 2 h with gradual increase of reaction temperatures from 25 °C to 200 °C, followed by addition of diamine V-4d. The resulting copolyimide V-5b was expected to be a nearly perfect alternating copolymer (with Ar₁ being *p*-phenylene, Scheme V.5). Finally, addition sequence of diamines V-4a and V-4d reversed and copolyimide V-5c (with Ar₂ being *p*-phenylene) was expected to be different from V-5b.

Copolyimide	Monomer Addition Sequence
V-5a	Add BNTDA, V-4a and 4d together.
V-5b	Add BNTDA and V-4a, r.t.- 200 °C in 2 h; then add V-4d.
V-5c	Add BNTDA and V-4d, r.t.- 200 °C in 2 h; then add V-4a.

Scheme V.5. Synthesis of copolymers by different monomer adding sequences.

V.4.2. Characterization of copolymers

The physical properties of three copolymers V-5a-c were listed in Table V.5. The three copolyimides V-5a-c showed different solubility in organic solvents and different T_g values (Table V.5). Copolymers V-5a and V-5c had better solubility than that of copolymer V-5b. Among three copolyimides, copolyimide V-5b had the highest T_g (319 °C) and the lowest solubility. The T_g (282 °C) of copolyimide V-5c was 37 °C lower than that of V-5b but was much more soluble. Apparently, the difference in T_g and solubility can be attributed to the different alternating sequences within the polymer mainchain that is caused by unsymmetric BNTDA. Copolyimide V-5a also showed the presence of a relatively high content of alternating sequence, as its T_g (312 °C) was close to that of alternating copolyimide V-5b.

Table V.5. Characterizations of copolyimides V-5a-c.

Polymer	η_{inh}^a dL/g	T _g ^b °C	T _d ^c °C	Solubility ^d			
				NMP	DMAc	TCE	CHCl ₃
V-5a	0.63	312	523	+	-	+	-
V-5b	N/M	319	511	±	-	±	-
V-5c	1.12	282	514	+	-	+	-

^a Inherent viscosity measured in NMP at 30 °C; N/M: Not measured due to low solubility in organic solvents listed in the table. ^b Obtained from the second DSC scan at a heating rate of 10 °C/min in nitrogen; N/O: Not observed. ^c 5% weight loss at a heating rate of 10 °C/min in nitrogen. ^d Measured at room temperature; Key: +, soluble; ±, partially soluble; -, insoluble.

V.5.Conclusions

Due to the different reactivity of anhydride group presented in BNTDA monomer, it was successfully used as end-capping agent to prepare oligomers with reactive end groups. Alternating block copolymers are readily prepared through these oligomers and the Tgs and thermal stability of these copolymers depend on the size of imide segments. In addition, the physical properties of copolyimides derived from BNTDA can also be tailored by monomer-adding sequence.

V.6.Experimental section

Materials

2,2'-Bis(4-[4-aminophenol]phenyl) propane (BAPP) and 4,4'-oxydiphthalic anhydride (ODPA) were purchased from Chriskev Company, Inc. and used without purification. Poly(1,4-butanediol) bis(4-aminobenzoate) (Mw = 834 g/mol) was obtained from Thomson Gordon Inc. in Burlington, Ontario, Canada. Pyridine, acetic anhydride, *m*-cresol and isoquinoline were purchased from Aldrich Chemical Co. and used without purification. N, N-Dimethylacetamide (DMAc) was vacuum distilled after drying over calcium hydride. Other solvents were used as received.

Model compound synthesis

To a flame-dried 50 mL, three-necked, round-bottom flask equipped with a nitrogen inlet/outlet and a magnetic stirrer, were added BAPP (0.2757 g, 0.6716 mmol), BNTDA (0.5000 g, 1.3430 mmol), 6 mL of DMAc and 5 drops of pyridine. The solution was stirred at room temperature under nitrogen overnight, then 5 drops of pyridine and 10 drops of acetic anhydride were added into the solution and raised the temperature to 60-70 °C and stirred overnight. The resulting solution was diluted with DMAc (5 mL) and poured into 200 mL of methanol. The yellow model compound was collected by filtration and washed with methanol several times. After drying at 100 °C for 24 h, model dianhydride was obtained in 92% yield. mp 281 °C (DSC); IR (KBr) 1782, 1744 and 1721 (naphthalic anhydride and phthalimide) and 1667 cm⁻¹ (C=O) (Figure 1, a); ¹H NMR (400 MHz, DMSO-d₆) δ 8.63 (d, 2 H, J = 7.48 Hz), 8.60-8.58 (dd, 2 H, J = 7.28,

0.88 Hz), 8.43-8.40 (dd, 2 H, $J = 8.55, 0.88$ Hz), 8.30-8.28 (dd, 2 H, $J = 7.77, 1.40$ Hz), 8.15-8.10 (m, 3 H), 8.05-8.04 (d, 2 H, $J = 7.48$ Hz), 7.95-7.91 (m, 3 H); 7.43-7.41 (d, 4 H, $J = 8.88$ Hz); 7.29-7.27 (d, 4 H, $J = 8.76$ Hz); 7.12-7.10 (d, 4 H, $J = 8.90$ Hz); 7.00-6.98 (d, 4 H, $J = 8.74$ Hz); 1.64 (s, 6 H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 194.60, 166.29, 160.50, 160.30, 156.83, 153.93, 145.92, 141.59, 140.91, 136.29, 135.65, 132.91, 132.53, 132.16, 131.32, 130.23, 129.12, 128.92, 128.68, 128.53, 128.30, 126.52, 124.16, 121.92, 119.81, 118.75, 118.49, 41.86, 30.69.

Preparation of imide oligomers end capped with BNTDA

The synthesis of imide oligomers end capped with BNTDA was carried out in 25 mL three-necked round-bottom flask equipped with a nitrogen inlet/outlet, condenser and a magnetic stirrer. Calculated molar quantities of each monomer (BAPP and ODPA) and catalytic amount of pyridine were charged and dissolved in DMAc to 20% solid contents. The solution was stirred at room temperature under nitrogen for 24 h, then excess of BNTDA was added into the solution and stirred another 8 h. After which time catalytic amount of pyridine and acetic anhydride were added into the solution and the reaction was heated up to 60 °C for 10 h, then cooled to room temperature and precipitated in methanol. The precipitate was filtered, washed with Soxhlet extraction apparatus overnight, and dried at 120 °C for 12 h. A specific example of imide oligomer end capped with BNTDA is given as follows:

A BNTDA-terminated imide oligomer V-2a (10710 g mol^{-1}) was prepared by charging a reaction flask with ODPA (0.8000 g, 2.5788 mmol), BAPP (1.1337 g, 2.7616 mmol) and dissolving in 10 ml of DMAc. After adding 5 drops of pyridine, the reaction

was stirred at room temperature for 24 h. Then, 0.15 g (0.4032 mmol) of BNTDA was added into the solution, and stirred for 8 h. Another 5 drops of pyridine and 10 drops of acetic anhydride were charged into the solution and heated up to 60 °C for 10 h. After cooling to room temperature, the reaction mixture was precipitated in methanol. After filtration, the solid oligomer was washed with Soxhlet extraction apparatus overnight and dried at 120 °C for 12 h. Yield = 92%.

General procedure for the synthesis of block copolymers.

One-step polymerization was used to prepare block polymer. The equivalent amount of BNTDA terminated imide oligomer was added under nitrogen into *m*-cresol solution of poly(1,4-butanediol)bis(4-aminobenzoate). The reaction was heated at 190-200 °C for 4-5 h, then precipitated in methanol and dried at 100 °C under vacuum for 10 h.

General procedure for the synthesis of copolymers by different monomer-adding sequences.

One-step polymerizations were used to prepare copolymers. The equivalent amount of BNTDA and two diamine monomers was added under nitrogen into *m*-cresol solution. The reaction was heated at 190-200 °C for 18-24 h, then precipitated in methanol and dried at 100 °C under vacuum for 10 h.

Instrument analysis.

The ^1H and ^{13}C NMR spectra were recorded on either a Varian Gemini-200 or a Bruker-400 instrument using tetramethyl silane as an internal reference. Infrared measurements were performed on a Bomen Michelson 120 FTIR spectrometer. Low- and high-resolution mass spectra were obtained on VG7070E and Kratos Concept 2H spectrometers, respectively. Elemental analyses were performed in the Guelph Chemical Laboratories Ltd., Guelph, Ontario, Canada. Melting points were taken from a Fisher-Johns melting apparatus or from a Seiko 220C differential scanning calorimeter (DSC) at a heating rate of 10 °C/min in nitrogen (200 mL/min). The apparent molecular weights of the polymers were determined by gel permeation chromatography (GPC) relative to polystyrene standards using chloroform at ambient temperature at a flow rate of 1.0 mL/min; a UV detector was set at 254 nm. Inherent viscosities were measured in CHCl_3 at 25 °C using an Ubbelohde dilution viscometer. The glass transition temperatures were determined on a Seiko 200 °C DSC at a heating rate of 10 °C/min in nitrogen (200 mL/min). Thermal stability, as measured by weight loss, of the polymer samples were determined using a Seiko 120TG/DTA analyzer from 25 to 700 °C at a heating rate of 10 °C/min.

V.7.References

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Contributions to knowledge

This thesis work on design and synthesis of new polyimides has demonstrated:

1. Introduction of naphthalimide moieties into polymer chain can dramatically increase the thermal stability.
2. Introduction of unsymmetric units into polymers can improve solubility of the resultant polymers, such as polymers derived from the unsymmetric dianhydride monomer displayed good solubility.
3. Naphthalimide-containing polymers are electroactive, electrochromic and potential candidates for electrochromic display applications.
4. Naphthalic and phthalic anhydrides in unsymmetric dianhydride monomer have different reactivity towards aromatic amines, and this specific monomer is useful to make oligoimides with active end-capped groups. These oligoimides with controlled physical properties are stable to moisture at room temperatures, but active to diamine monomers or amine end-capped oligomers at high temperatures to form block copolyimides.

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